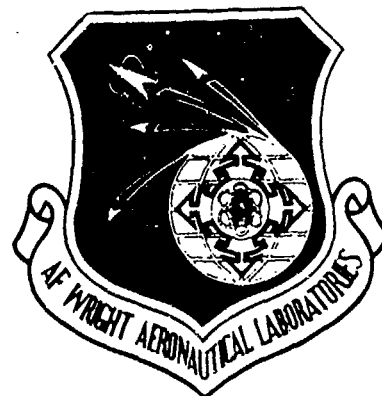


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MASS SPECTROMETRIC MEASUREMENTS OF COMBUSTOR SPECIES IN  
RAMJET COMBUSTION SYSTEMS

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## I. INTRODUCTION

For several years, the Ramjet Technology Branch of the Aero Propulsion Laboratory (APL) has conducted a research program in the area of advanced ramjet combustion. A major goal of this research has been to achieve a better combustor design for volume-limited ramjet missile applications. Several previous studies<sup>1-3</sup> conducted by AFAPL have utilized dump combustors, under both real and simulated combustion conditions. The effects of numerous factors, including the combustor configuration, and the types of flame holder and swirler, as well as the operating conditions (fuel-air ratios, inlet gas temperature and pressure, fuel types, and other factors) on the over-all combustion efficiency were evaluated in these earlier investigations. Detailed characterization of the combustor flowfield was also accomplished in several cases.

In carrying out the above-described research programs, a number of test facilities and advanced diagnostic techniques were employed to produce experimental test data pertinent to both current and long-range technology programs for the development of advanced ramjet combustors. One of the instrumentation systems used for diagnostics is a mass spectrometric gas monitoring system which has been used for in-situ measurement of gas species concentrations in combustor flowfields. This system was successfully interfaced with a cold flow dump combustor in order to monitor concentrations of air and a simulated fuel (Argon) within the combustor flowfield. In the course of this project, this system has been employed to obtain extensive simulated fuel

concentration profile data<sup>10-12</sup> which contributed significantly to the characterization of the combustor flowfield. This data is important for elucidating the dynamic fuel-air mixing mechanism, as well as for theoretical modeling studies aimed at improving fuel-air mixing in the combustor.

In 1981 a new contractual research effort supported by APL at Wright State University was initiated. Part of this effort was an extension of previous APL-funded contractual research programs for in-situ measurement of fuel/air mixing profiles in the ramjet combustor flowfield. However, the principal objective of this new research program was to develop a new experimental system for in-situ measurement of gaseous species in a reactive ramjet combustor. This entailed design and development of new gas sampling and gas detection systems, both of which constituted major efforts.

The present report summarizes the accomplishments under this contract for the period of September 12, 1981 to September 30, 1985. In view of the diverse nature of various portions of the work described herein, this report is presented in four parts. In the following section (Section II), the design, fabrication and evaluation of an improved gas sampling probe system for reactive ramjet combustor gas sampling are discussed. The next section of the report (Section III) describes progress in the development of batch combustor sampling and methodology for analyses of these samples. In Section IV of this report, the construction of a novel molecular beam mass spectrometric gas monitoring system is described. Results of several initial tests



with this new system are also reported. Finally, Section V of the report summarizes the results of a series of in-situ measurements of the simulated fuel/air mixing profiles in the ramjet combustor flowfield using a dual-inlet ducted rocket combustor.

## II. DESIGN, FABRICATION AND EVALUATION OF AN IMPROVED GAS SAMPLING PROBE SYSTEM

### A. Description of the Probe Design

The initial task of the present project entailed the design, fabrication, and evaluation of an improved gas sampling probe system for ramjet combustor sampling. The preferred gas sampling probe incorporates a quartz tip for gas sampling and a water-cooled stainless steel body, which provides the necessary physical strength and protection for the quartz probe orifice. When properly designed, a probe of this type should have the desired physical strength, chemical inertness, cooling, and resistance to soot formation and accumulation, while simultaneously minimizing adverse aerodynamic, thermal, and chemical effects on the sampled gas.

Figure 1 is a schematic diagram of a new gas sampling probe system which satisfies the criteria just mentioned. The design of this system is based on an earlier prototype which was designed and fabricated during a previous contract, and which proved to be quite successful when tested in an actual ramjet combustor sampling experiment<sup>1,2</sup>. However, the system shown here (Figure 1) incorporates several important improvements with respect to the previous model, as will now be discussed.

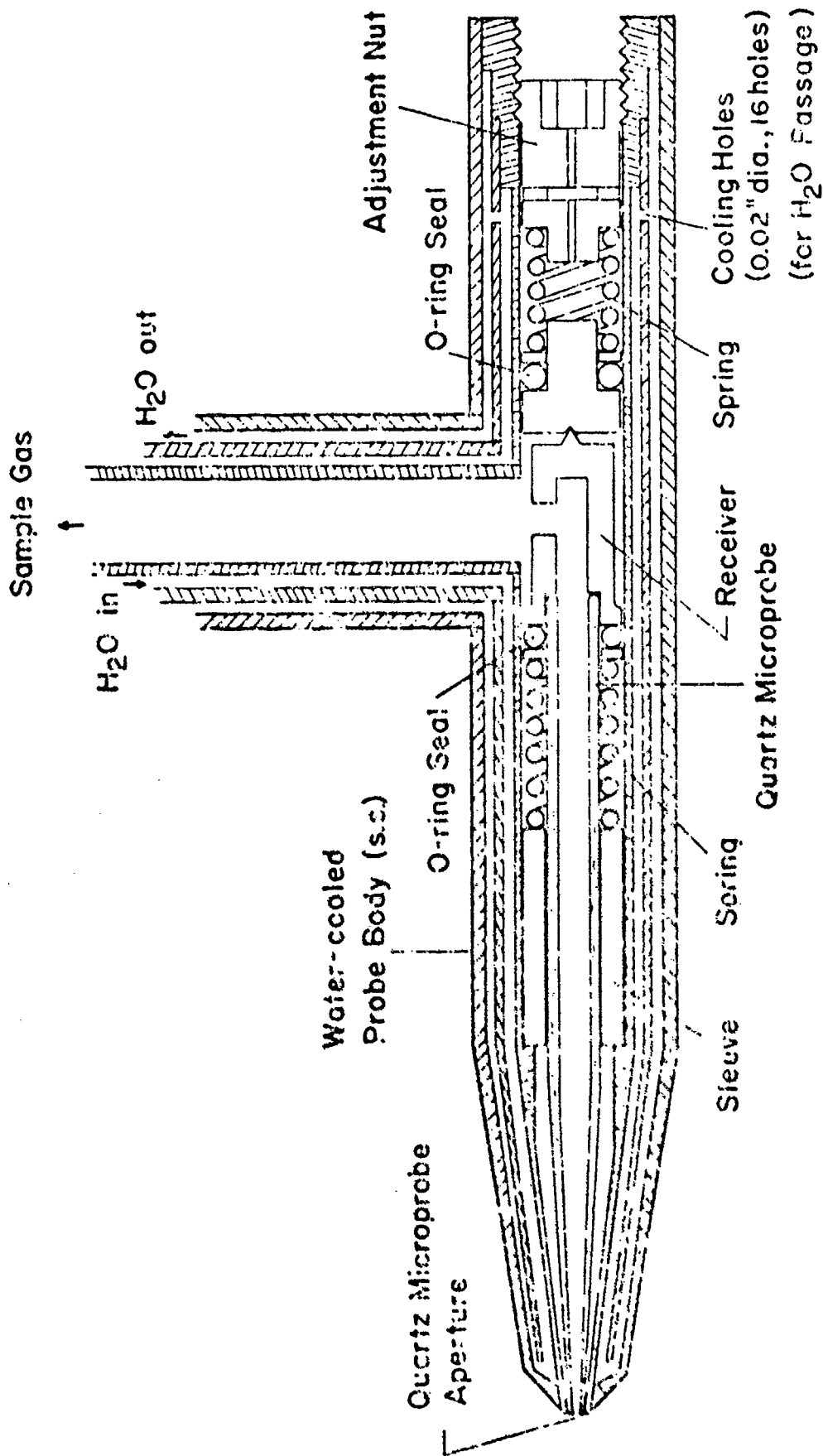


Figure 1. Schematic Diagram Of The New Gas Sampling Probe Assembly

As seen from Figure 1, the new gas sampling probe system consists essentially of three components: a) a quartz microprobe; b) a water-cooled stainless steel probe body; and c) an internal mounting assembly. The probe body (total length 3 inches; OD 0.5 inch) is formed from three concentric tubes which are joined, at right angles, to three other concentric tubes. The front portion of the probe body is a two-sectioned cone with an aperture (1 mm diameter) located at its front end. The inside cavity of this probe body, (with an internal diameter of 0.25 inch in the straight portion), houses the quartz microprobe and the internal mounting assembly. The circulation of cooling water through the probe is such that approximately 60% of the total water flow passes through the front end of the probe body, while the remaining 40% passes through the rear end of the probe.

The quartz microprobe is simply formed from a quartz tube (3 mm outside diameter, 2 mm inside diameter) which is tapered down to a cone at its front end. It has a sonic orifice, the diameter of which ranges from several microns to 0.1 mm or more, depending on the application. When the probe is assembled, it is preferable that the front end of the quartz microprobe extends outward from the probe body by a distance of at least 0.5 mm or more, in order to minimize the disturbance (aerodynamic, thermal, chemical) of the sampled gas. Such disturbances are expected to occur, especially in the immediate vicinity of the surface of the probe body. The extent to which the quartz tip section will actually extend from the probe body will be experimentally determined, on the basis of the cooling rate of the quartz

microprobe (cooling occurs through the glass-metal contact point at the probe body orifice) and the physical strength of the quartz material.

The internal mounting assembly includes a sleeve, front and back springs, front and back O-ring (viton), a quartz tube receiver, plugs, washers and an adjustment nut (made of inconel). This assembly has two functions: 1) to provide a tight seal between the quartz microprobe and the probe body; and 2) to provide an optimum pressure at the glass-metal contact in order to maximize the cooling of the quartz tip. During assembly of the probe, the adjustment nut is tightened, which causes the front and back springs to be equally compressed, until the quartz tip is in firm contact with the probe body orifice. This compression causes sealing to be achieved at the front and back O-rings. The adjustment nut is then further tightened, which causes further compression of only the back spring. This additional compression results in the application of pressure at the glass-metal interface. The heat transfer rate through this contact point can be easily enhanced by several orders of magnitude by increasing this contact pressure. The exact pressure applied to the quartz microprobe, as well as to the front and back springs, can be calculated. The pressure can be readily varied by changing the dimensions of the quartz microprobe and/or the types of the springs.

In summary, the design of the present probe system presents several significant improvements over the previous prototype. Among these improvements are: 1) a better glass-metal sealing

arrangement; 2) a much higher cooling rate of the quartz microprobe tip; 3) greater simplicity of the configuration and better interchangeability of the quartz microprobe; 4) a five-fold increase in the cooling water flow rate; and 5) the modular concept of the design permits easy repair of probe defects.

#### B. Probe Fabrication and Evaluation

A prototype based on the design in Figure 1 was fabricated and assembled. Figures 2-6 are various photographs of this prototype sampling probe. The photograph in Figure 2 was obtained prior to assembly of the probe, and shows the details of the internal components of the probe. Figure 3 shows the entire probe, as mounted on a flange. Figure 4 is a close-up view of the front portion of the probe, while Figures 5 and 6 are enlarged views of the probe, showing the details of the quartz microprobe tip. The diameter of the quartz aperture is approximately 0.22 mm (0.009"). The quartz tip extends from the probe body a distance of 0.18 mm.

The assembled probe was subsequently subjected to a series of evaluation tests. The first was a leak test. In this test, a quartz probe with a blind tip was installed in the assembled system while the outlet end of the probe was connected to a pumping system. The assembly was found to be leak-free. However, due to the large variation which occurs in the size of commercially available quartz tubes, (3.0 mm  $\pm$  0.5 mm), careful selection of tubes for use as probes is required. A second set of the internal mounting assembly components was subsequently fabricated to accommodate this size variation.

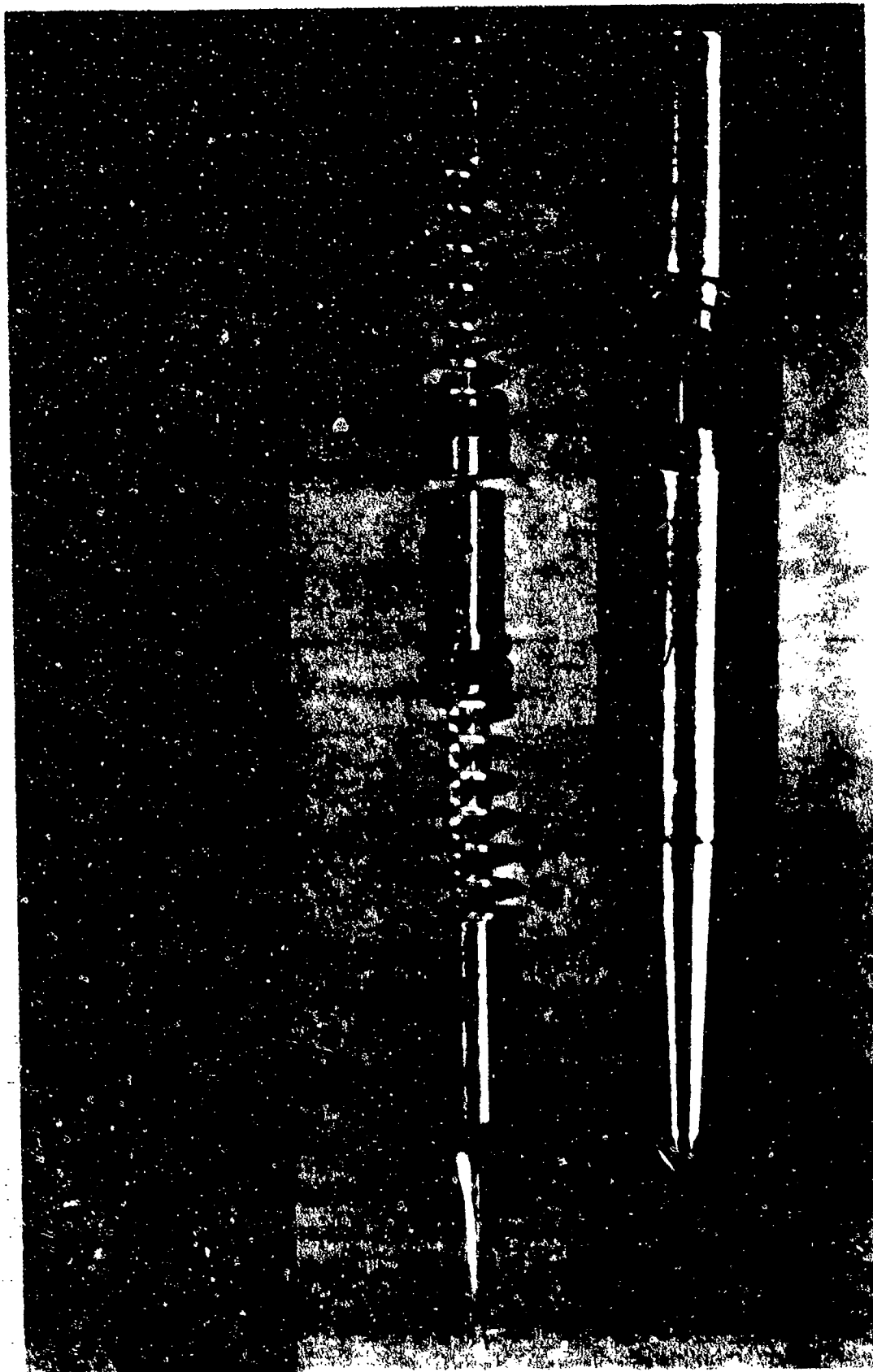


Figure 2. Photograph of the quartz/stainless steel sampling probe prior to assembly.

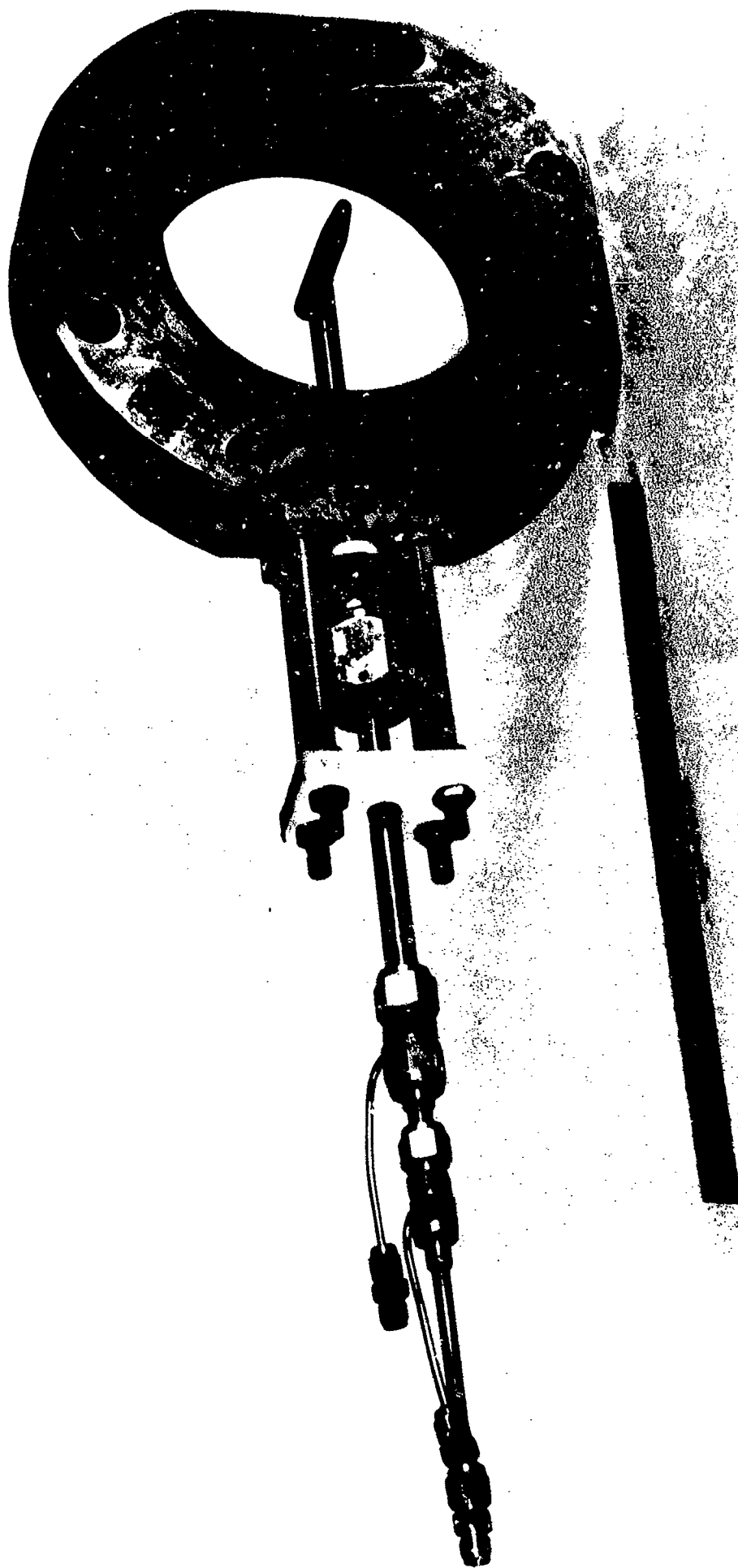


Figure 3. Photograph of the quartz/stainless steel sampling probe as mounted on the probe flange.

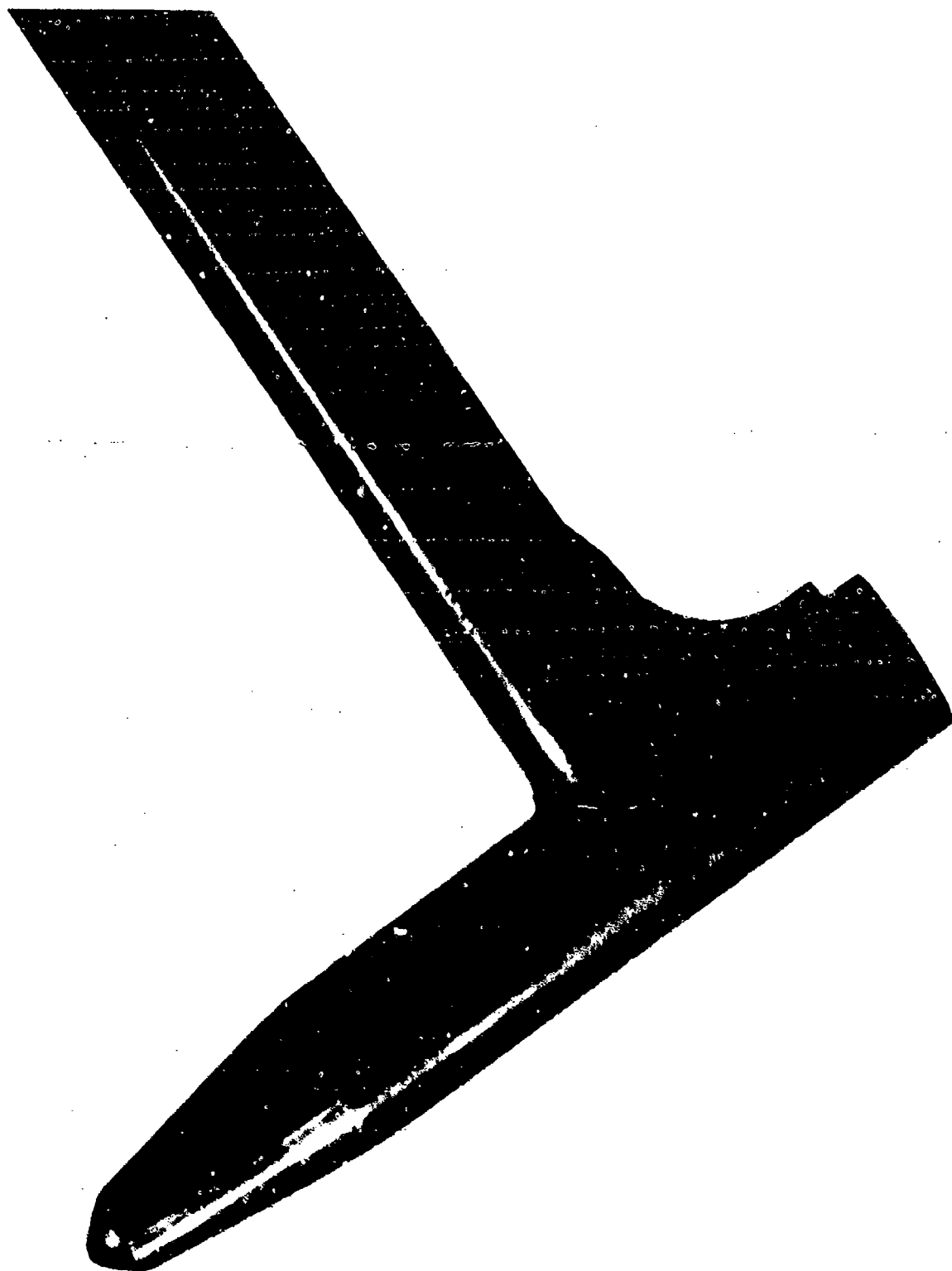


Figure 4. Photograph of the probe body section of the quartz/stainless steel sampling probe.





Figure 5. Photograph of the front tip portion of the quartz/stainless steel sampling probe.



Figure 6. Photograph of the quartz tip of the quartz/stainless steel sampling probe.

The second probe evaluation test accomplished was for the purpose of evaluating the cooling water recirculation. The attainable cooling water flow rate at 50 psig water head pressure was found to be 740 mL/min. This is approximately four times the water flow rate which was attained in the first prototype gas sampling probe (200 mL/min at 50 psig) having the same overall probe dimensions. The water flow rate with the present probe was increased to 2900 mL/min when a maximum water head pressure of 125 psig was applied. No water leaks were detected in this test. The split of the cooling water between the front and back sections of the probe was experimentally determined to be in a 60:40 ratio, which is in reasonable agreement with the calculated estimate of 66:34.

The final test accomplished with the probe evaluated the tolerance of the probe body and the quartz tip to high temperature heating. This was achieved by heating various parts of the probe system with a methane-oxygen torch, which is known to yield a temperature as high as 2000°C, at its hottest flame zone. The first torch test was done on the probe body itself without the quartz microprobe. The cooling water head pressure was adjusted to 50 psig. The torch was adjusted to yield either a small, medium or large flame. This flame was then brought into direct contact with various sections of the probe body. No surface discoloration was observed when the small and medium flames were applied to the body. However, application of the large torch flame resulted in two surface areas gradually becoming dull red upon persistent heating. One of those areas

was the back surface of the end of the probe body, and the adjustment nut. This is the area most susceptible to temperature rise because it is located at a relatively long distance from the circulating water (Figure 1, 16 water passage holes). There is no easy solution to this problem, but fortunately, since this area is located on the back side of the probe, much less heating of this surface is anticipated when the probe is inserted into the ramjet combustor. The second area of the probe assembly which showed discoloration upon intense heating was the probe body surface directly opposite the T-intersection. This suggests that the flow of cooling water beneath this area must be stagnant. This problem could likely be solved by drilling a relief hole in the middle stainless-steel layer to increase the water circulation. This has not yet been accomplished, but may be necessary if the actual ramjet combustion tests indicate excessive heating of this area of the probe.

The next probe component which was tested with the torch was the quartz microprobe tip which extends from the probe body. It is desirable that this tip be extended a distance of 0.5 mm or more so that the influence of the probe body (which is relatively cold and massive) on the sampling zone (immediately in front of the quartz probe orifice) is minimized. An extensive series of torch tests of the probe tip was accomplished in which the quartz extension was varied from zero to 0.5 mm; the orifice size was varied from 0.03" to 0.15"; and the glass to metal contact pressure was varied from 0.5 to 1.5 lb. It was found that the maximum allowable extension of the tip was 0.34 mm when the probe

tip was exposed to the large flame for 1 minute. Exposure for longer periods resulted in distorting or melting the probe tip. This finding was somewhat disappointing and is believed to be inherently due to the poor heat transfer capacity of quartz. Nevertheless, this result represents a significant improvement over the state-of-the-art in minimizing undesirable effects of probes on the sampling zone.

### III. DEVELOPMENT OF BATCH COMBUSTOR SAMPLING AND METHODOLOGY FOR ANALYSES OF BATCH COMBUSTOR SAMPLES

#### A. Batch Combustor Sampling

Prior to the construction of an in-situ, on-line mass spectrometer gas sampling system for use with the ramjet combustor, we considered it advisable to conduct several preliminary combustor sampling tests in an off-line analysis mode. For these experiments, we intended that gases from the combustor would simply be sampled through the sampling probe and collected in a bottle with a valve. These would later be transported to the mass spectrometer analysis system and analyzed. Compared with on-line sampling, the analysis of batch samples collected off-line is more tedious and subject to much greater error. Therefore, we planned for this type of analysis to be conducted on a short term basis, for the purpose of evaluating the overall performance of the sampling probe system rather than obtaining an accurate quantitative analysis of the combustor species.

Figure 7 shows a schematic diagram of a portable batch

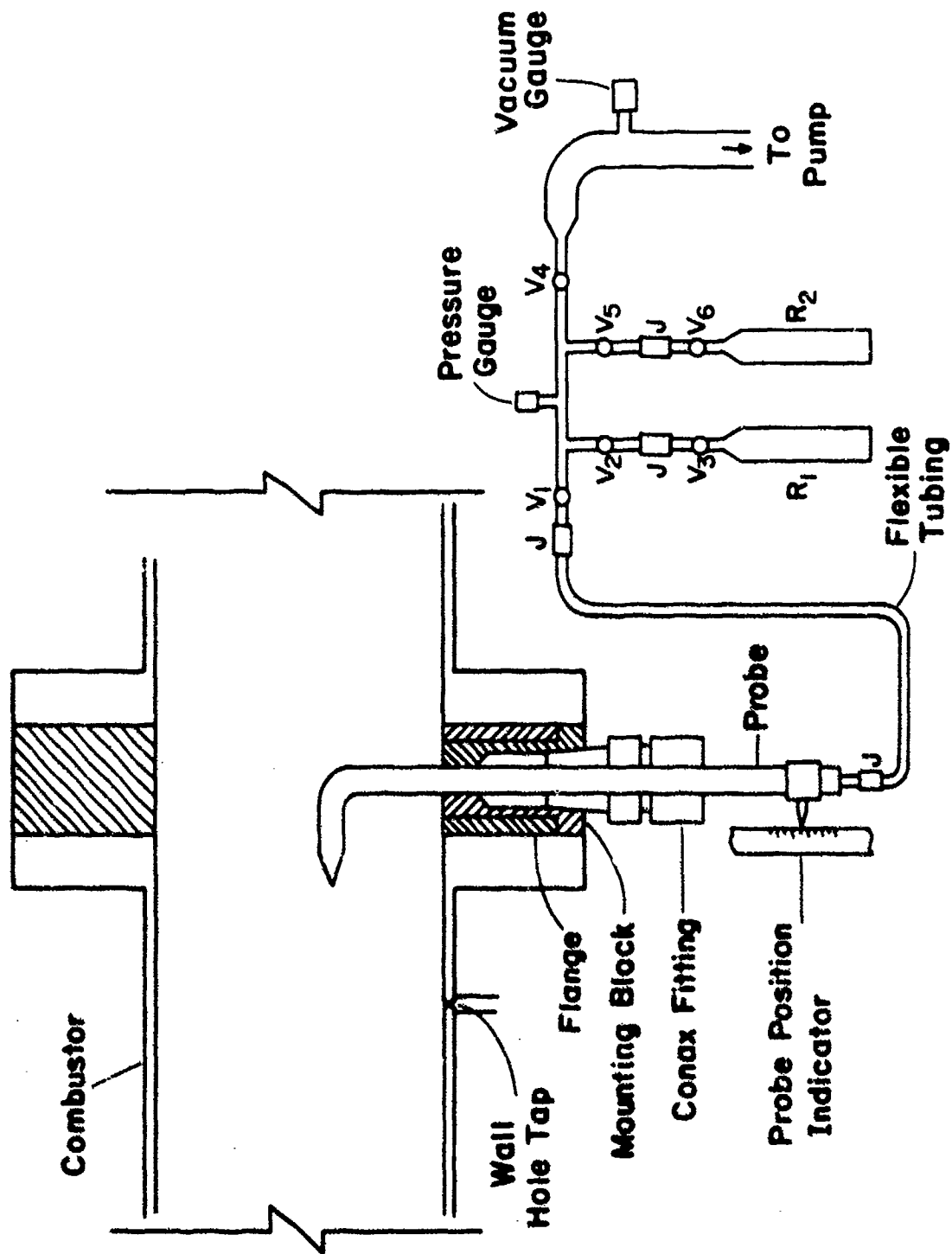


Figure 7. Schematic Diagram of the batch combustor sampling system

sampling system which was constructed during the previous contracting period<sup>1</sup>, and was further modified recently. In this system, the sampling probe is mounted on a flange which is inserted between two sections of the ramjet combustor. The lower end of the sampling probe is connected to a vacuum system. This vacuum system incorporates a mechanical pump, vacuum joints, solenoid valves, a pressure gauge and two reservoirs for collecting the sampled gases. For water-cooled sampling probes, a distilled water cooling system is also provided, which consists of a twenty-gallon water reservoir, water pump and motor, water pressure gauge, safety switch, flow meter, filter and plumbing lines.

Prior to the actual probe sampling test of the combustor, a simulated probe test was first carried out in which a dummy probe was utilized instead of the real sampling probe. The objective of this test was to discover any possible defects in the overall probe-combustor interface system and to specifically evaluate the adequacy of the cooling-water circulation system. The dummy probe employed for this purpose is shown schematically in Figure 8. (The items listed by number in the following refer to corresponding numbers on the schematic.) This probe consists mainly of an outside tube, 1, (S.S. 1/2" OD) and an inside tube, 2, (S.S. 3/8" OD) which are concentrically joined together with a Swagelok joint. The front end of the outside tube, 1, is sealed (silver solder) with an end cap, 3. Cooling water is allowed to circulate through tubes 1 and 2. As many as five iron-constantan thermocouple wires (1/16" OD), 7 to 11, can be inserted into the

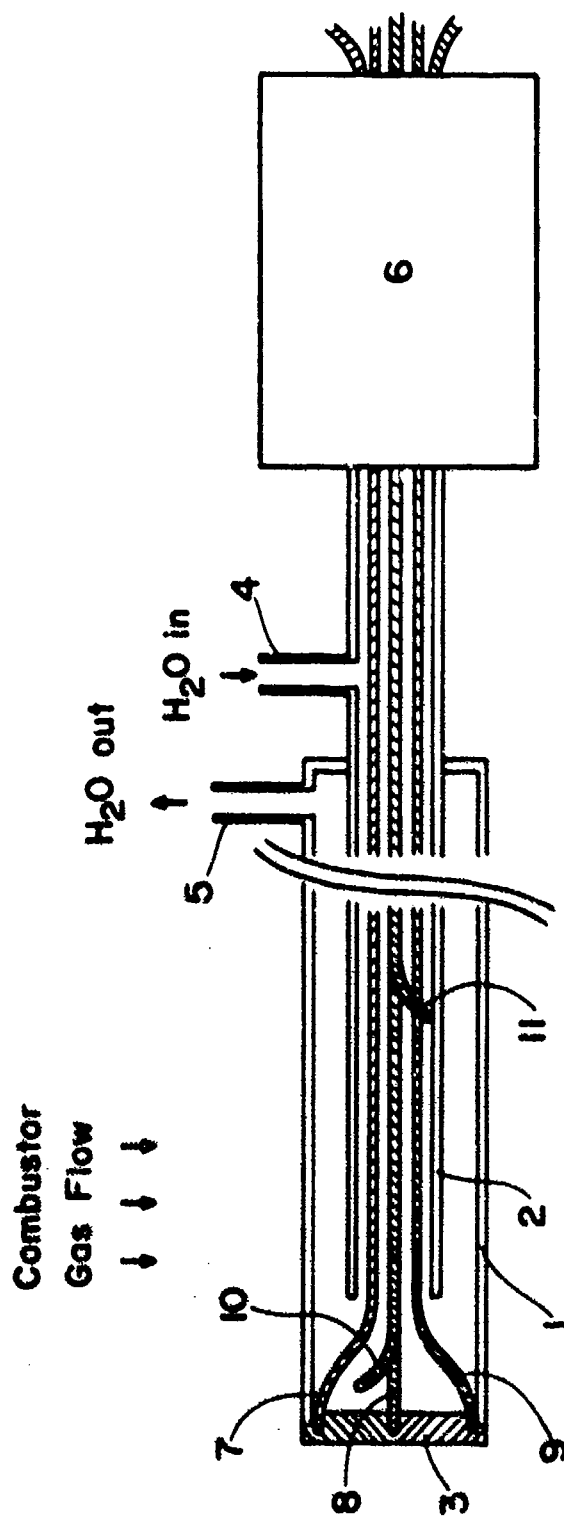


Figure 8. Schematics of the Dummy Probe: 1) Outer tube  $\frac{1}{2}$ " OD; 2) Inner tube  $\frac{3}{8}$ " OD; 3) end cap; 4) water inlet tube; 5) water outlet tube; 6) Conax 5-hole gland; 7-11) Iron-constantan thermocouple wire  $\frac{1}{16}$ " OD.



probe. The temperature sensing tips of the wires, 7, 8, and 9, are inserted and secured into the end cap, 3, with silver solder, in order to measure the probe wall temperature during ramjet combustion tests. The wires, 10 and 11, are freely suspended to measure the temperature of the circulating water.

Four different ramjet combustion tests were accomplished using the dummy probe. The ramjet combustor facility employed includes a combustor section (15 inch x 6 inch I.D.) with two rectangular side inlet ports. The dummy probe was mounted on the probe flange (Figure 3), which was placed at the end of the combustor section. On the down stream side of the probe flange was a nozzle section of 4.24 inch I.D. In all four tests, the air mass flow was maintained constant at 3.95 lbs/sec while the fuel (JP-4)/air ratio was varied between 0.039 and 0.059. The combustor temperature derived from thrust measurements ranged from 2896 to 3817 °R, while the combustion efficiency was found to vary from 82% to 87%. The exit nozzle pressure was varied up to 33 psia.

During these tests, the cooling water was allowed to circulate through the dummy probe at a flow rate of 3.0 liters/min. The temperatures of the probe at various points were monitored continuously, and recorded by the interfaced computer system. The duration of each test was typically 30 seconds.

The test results demonstrated that the cooling of the dummy probe was quite adequate. The rise in the cooling water temperature was less than 100°F. The maximum registered probe wall temperature (detected by thermocouple wire 7, Figure 8) was

1447°R, with the combustor temperature being 3817°R. After the test, the entire assembly was readily disassembled with no difficulty. However, a small water leak was observed at the probe silver solder joint. This may have been caused either by an initial fabrication defect or by a temperature excursion in the outside wall, which exceeded the melting point of the silver solder (approximately 1800°R).

After the completion of the dummy probe ramjet combustion tests, the quartz S.S. sampling probe was next tested under actual ramjet combustion sampling conditions. This was the ultimate test of the performance of the sampling probe. The ramjet combustor facility employed here was the same as that described for the dummy probe tests. The sampling probe was also mounted on the probe flange with the probe body section aligned with the combustor center line. The pressure of the collected gas was monitored continuously during each test. The circulating cooling water flow rate was set at 2.9 liters/min for these tests. The temperature of the outlet water was also monitored continuously to determine the water temperature rise which occurred during each sampling test.

A total of four sampling tests were conducted. Table 1 lists the operating conditions of the ramjet combustor and the sample probe parameters recorded during these tests. Again, the observed rise in the cooling water temperature was small. Figures 9-11 are photographs of the probe after it was removed from the ramjet combustor. The surface of the stainless-steel probe body was still shining and clean after the tests. The

TABLE I  
OPERATING CONDITIONS OF THE RAMJET COMBUSTOR DURING PROBE SAMPLING TESTS

Test No.	Fuel/Air Ratio	Combustor Temp. (°F)	Exit Nozzle Pressure (psia)	Sampling Period (sec)	Final Sample bottle press. (psia)	Cooling Water Temperature Rise (°F)
1	0 (hot air only)	1167	11.4	40		7
2	0.035	3093	18.7	21	1.8	39
3	0.035	3021	18.7	28	3.4	36
4	0.048	3495	18.8	21	1.8	44

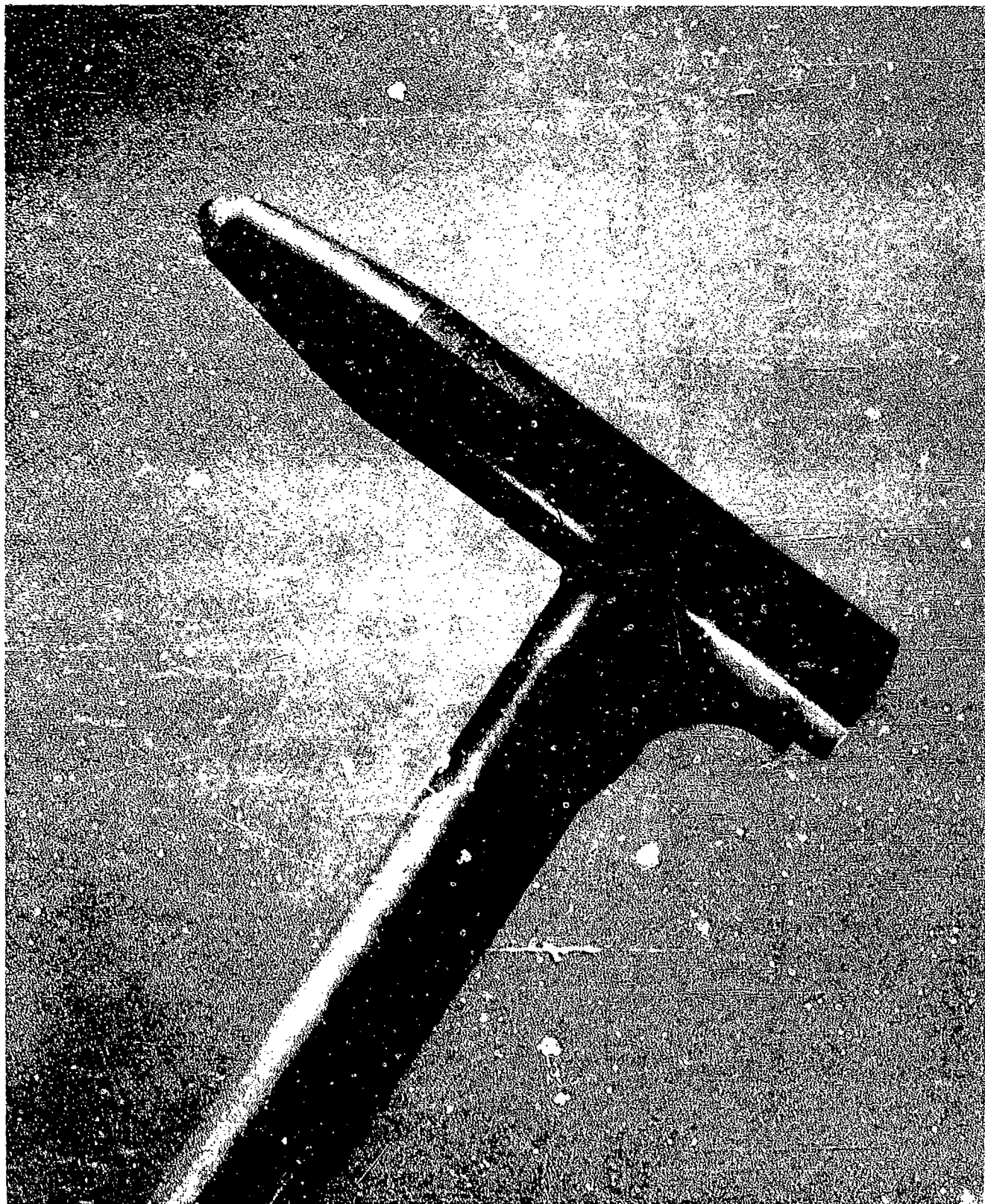


Figure 9. Photograph of the quartz/stainless steel sampling probe after ramjet combustion sampling tests.



Figure 10. Photograph of the quartz/stainless steel sampling probe (front tip portion) after ramjet combustion sampling tests.



Figure 11. Photograph of the quartz/stainless steel sampling probe (quartz tip portion) after ramjet combustion sampling tests.

surface of the quartz tip was slightly dusted with a layer of soot following the tests, but no observable distortion or damage was observed. The diameter of the quartz aperture was still approximately 0.22 mm and the tip extension length was 0.18 mm after the tests, the same as those parameters were prior to the combustion tests.

B. Development of the Methodology for Batch Combustor Sample Analysis

The chemical compounds that are typically present in a batch combustor sample include  $N_2$ ,  $O_2$ , CO,  $CO_2$ ,  $H_2O$  and the unburned fuel. The best procedure for the mass spectrometric analysis of these species entails the use of selected-ion-monitoring, in which ions that are characteristic of these species are monitored, in rapid sequence. In principle, this permits simultaneous detection and quantitation of all these species for each gas sample collected. The selected-ion-monitoring mass spectrometric technique is not only suitable for the analysis of batch combustor samples, but can also be applied (with some modifications) for the on-line combustor samples to be analyzed with the molecular-beam mass spectrometer.

Table 2 lists a total of twelve ions that can be monitored in the current selected-ion-monitoring mass spectrometer operating mode. Generally speaking, the analysis of  $N_2$  (based on the ion signal at  $m/z$  28);  $O_2$  (based on the ion signal at  $m/z$  32);  $CO_2$  (based on the ion signal at  $m/z$  44); and  $H_2O$  (based on the ion signals at  $m/z$  17 and 18) are straightforward and are not expected to present significant difficulty. As seen in this

TABLE 2  
PARAMETERS FOR MULTIPLE ION MONITORING OPERATION OF THE  
MASS SPECTROMETER

Channel No.	m/z	Ions	Source
1	14	$N^+$ , $CH_2^+$	$N_2$ , JP-4, Air impurity
2	15	$CH_3^+$	JP-4, Air impurity
3	17	$OH^+$	$H_2O$
4	18	$H_2O^+$	$H_2O$
5	28	$N_2^+$ , $CO^+$ , $C_2H_4^+$	$N_2$ , $CO$ , $CO_2$ , JP-4
6	32	$O_2^+$	$O_2$
7	44	$CO_2^+$	$CO_2$
8	57	$C_4H_9^+$	JP-4 (paraffins, linear)
9	69	$C_5H_9^+$	JP-4 (paraffins, linear, cyclic)
10	70	$C_5H_{10}^+$	JP-4 (paraffins, linear, cyclic)
11	77	$C_6H_5^+$	JP-4 (aromatics, benzene)
12	91	$C_7H_7^+$	JP-4 (aromatics)



table, the ions at  $m/z$  57, 69, 70, 77 and 91 are proposed as indicators of the JP-4 fuel. JP-4 is known to have an average molecular weight of 128, but this fuel actually consists of literally hundreds of chemically distinct components. These components are largely of two types, the first being paraffin hydrocarbons, including both linear chain ( $C_nH_{2n+2}$ ,  $n = 4$  to 18) and cyclic compounds ( $C_nH_{2n}$ ,  $n = 4$  to 18). The second type of components in this fuel is aromatic hydrocarbons ( $C_nH_{2n-6}$ ,  $n = 6$  to 18). Monitoring the above indicated set of five ions will provide information on the levels of fuel components of each of these types, while the sum of these ions is representative of the concentration of total hydrocarbons, and is indicative of the unburned fuel in the sample.

The only major compound of interest in the combustion gases that is not mentioned in Table 2, and thus cannot be successfully analyzed by the selected-ion-monitoring procedure described above, is CO. Under typical electron impact ionization conditions, CO molecules can yield ion signals at  $m/z$  28, ( $CO^+$ ), at  $m/z$  12, ( $C^+$ ), and  $m/z$  16, ( $O^+$ ) in the mass spectrum. Unfortunately, none of these ions can be utilized for the detection of CO, owing to the presence of other interfering ions at these masses which are produced by other species. These interfering ions are either ions of exactly the same species, but arising from different molecules (for example  $C^+$  from  $CO_2$ ;  $O^+$  from  $O_2$ ), or ions of the same nominal mass which are not resolved, under normal low resolution mass spectrometric conditions, from the ions produced by CO (for example,  $N_2^+$  which

arises from  $N_2$  at  $m/z$  28). For this reason, we planned that detection of CO in the batch sample will be accomplished in a separate measurement using a gas chromatograph-mass spectrometer (GC-MS) system, as described in a later section of this report.

Shown in Figure 12 is a schematic of the sample inlet system housed in an oven which has been extensively modified to accommodate the analysis of batch samples by GC-MS or MS. The system includes the GC column, two sample bottles, standard liquid and gas injection ports, a U-trap, and an eight-port valve which is equipped with two calibrated-volume sample loops. The operation of these components will be described later in association with the discussion of the methodology utilized.

The experimental procedure begins with placing the sample bottle (r1) containing the collected ramjet combustor sample in the oven as shown in the schematic. All gas lines inside the oven are subsequently evacuated using a vacuum pump. The second bottle (r2), which has the same volume (300 mL) as the other sample bottle (r1), is also evacuated. The temperature of the oven is then raised to 150°C, or higher if necessary, to ensure that all condensable species (water, fuel, etc.) in the bottle r1 are vaporized. When the oven temperature is stabilized, the valves V11 and V12 are momentarily opened and closed, which allows the ramjet sample to be equally distributed between the two bottles (r1 and r2). The residual gas within the gas lines is then pumped away.

As seen in the figure, the second bottle (r2) is fitted with an injection port (m3) which permits injection of known

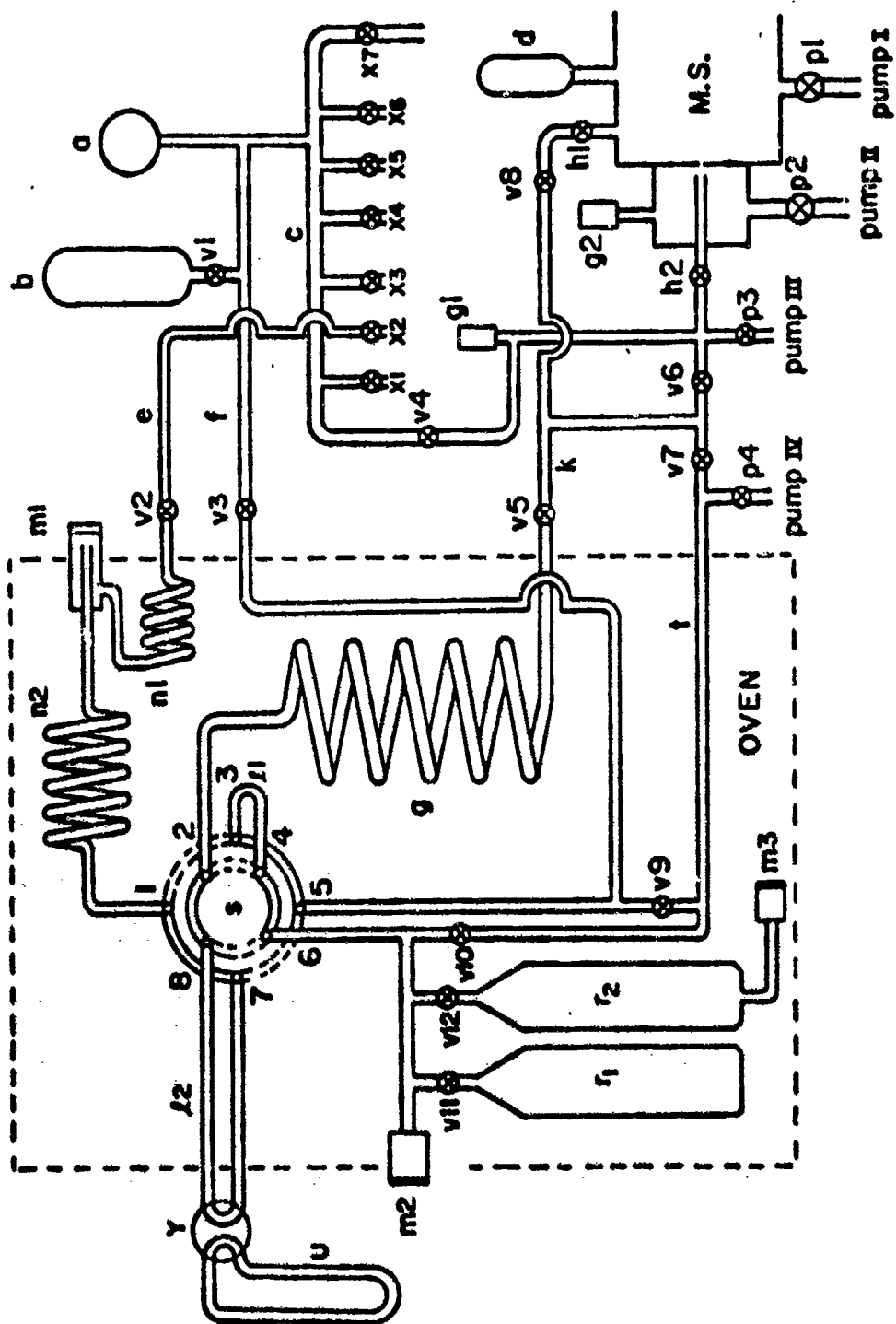


Figure 12. Schematic diagram of the batch ramjet sample analysis system.

quantities of standard gases and liquids into the bottle, r2. These injected gases and liquids serve as the internal calibration standards, which are used to achieve more accurate analyses of the ramjet sample.

As discussed previously, all of the ramjet sample components except CO can be analyzed directly using selected-ion-monitoring mass spectrometry. With this method, the sample and/or standards in the bottles r1 and r2 are slowly admitted into the mass spectrometer through valves V10, V7, V8, and metering valve h1. The output signal responses at the various ion masses which are monitored can be readily displayed on a multi-channel oscillograph recorder and acquired by the interfaced computer. An interactive computer program has been written to accomplish signal averaging and background subtraction for quantitating these ion signal responses.

The analysis of CO in the batch ramjet sample is achieved by gas chromatographic (GC) separation of the components of the combustion products, followed by mass spectrometric selected-ion-monitoring detection of the CO components. The GC column used here is a 12-ft x 1/8-inch-OD stainless steel tube, filled with molecular sieve 13x, and the column is operated at ambient temperature. This column will separate CO from all of the other components ( $N_2$ ,  $CO_2$ ,  $O_2$ , fuel) that may interfere with the mass spectrometric detection of CO.

To initiate the GC-MS analysis, a carrier gas (He) is allowed to flow successively through the valve, V2, the loops, n1 and n2, the eight-port valve, (s), the GC column, g, the

valves, V5, V6, and h2, and finally into the mass spectrometer ion source. The throttling valves, P2 and P3, can be adjusted to produce an appropriate ion source pressure for a given carrier gas flow rate.

The eight-port valve, S, is a two-way valve specially designed to deliver a given quantity of gas sample for GC analysis. The quantity of sample delivered is controlled by the volume of the sample loops L1 and L2, and the sample pressure. If the valve is initially turned to the first position, the gas flow inside the valve will be along the path of the solid line, as shown in the schematic. In this position, the carrier gas enters at port 1 and exits at port 7, then flows through loop L2, enters again at port 8, and exits at port 2 into the GC column. At the same time, the internal channels bound by the ports, 4 and 6, 3 and 5, as well as the loop, L1, are pumped down to vacuum by opening valves V9 and/or V10. Once vacuum is achieved, valves V9 and V10 are closed, and loop L1 is then ready to receive the sample from the sample bottles, r1 or r2. After sample introduction, the eight-port valve, S, is switched to the second position, after which the gas flow within the valve will follow the path of the dashed line shown in the schematic. The sample which is present within the loop, L1, will then be swept by the carrier gas into the GC column for analysis. Concurrently, the second loop, L2, will be pumped down to vacuum, and will then receive the next aliquot of the gas sample. It is clear that by alternate switching of the eight-port valve, S, in conjunction with operation of the valves V9, V10, V11 and V12, any desired

number of GC-MS analyses can be achieved for each sample collected from the ramjet combustion test. Of course, the quantity of sample introduced into the loops L1 and L2 after each successive analysis cycle will be reduced due to the progressive reduction in the pressure in the sample bottle.

Figure 13 shows the GC-MS output for CO, as plotted by the interfaced computer system in an actual test. The three traces shown correspond to the signals for the three ions monitored, which are  $m/z$  28 ( $N_2^+$  from  $N_2$ ,  $CO^+$  from CO);  $m/z$  14 ( $N^+$  from  $N_2$ ); and  $m/z$  12 ( $C^+$  from CO). The mass peaks for  $N_2$  (at 51 sec) and CO (at 93 sec) are well separated. Quantitative calibration of the apparatus for CO can be obtained by using either the  $CO^+$  or  $C^+$  signal response.

The task of quantitatively calibrating the detection system for determination of the species  $N_2$ ,  $O_2$ ,  $CO_2$ , CO, JP-4 fuel, and  $H_2O$  in the batch sample was also largely completed during this project. Calibration curves, in which the relative ion intensities characteristic of each component were plotted against the relative mass fraction of that component (relative to  $N_2$ ) were obtained. The mass spectrometric responses for all of these gases (except  $H_2O$ ) were found to be linear within the concentration ranges of interest. The less-than-ideal response observed for  $H_2O$  was mainly due to insufficient vaporization and equilibration of the water in the sample bottle, and to the steadily increasing water vapor background pressure in the mass spectrometer. Further work is required to solve this problem.

The methodology described above was next applied for the

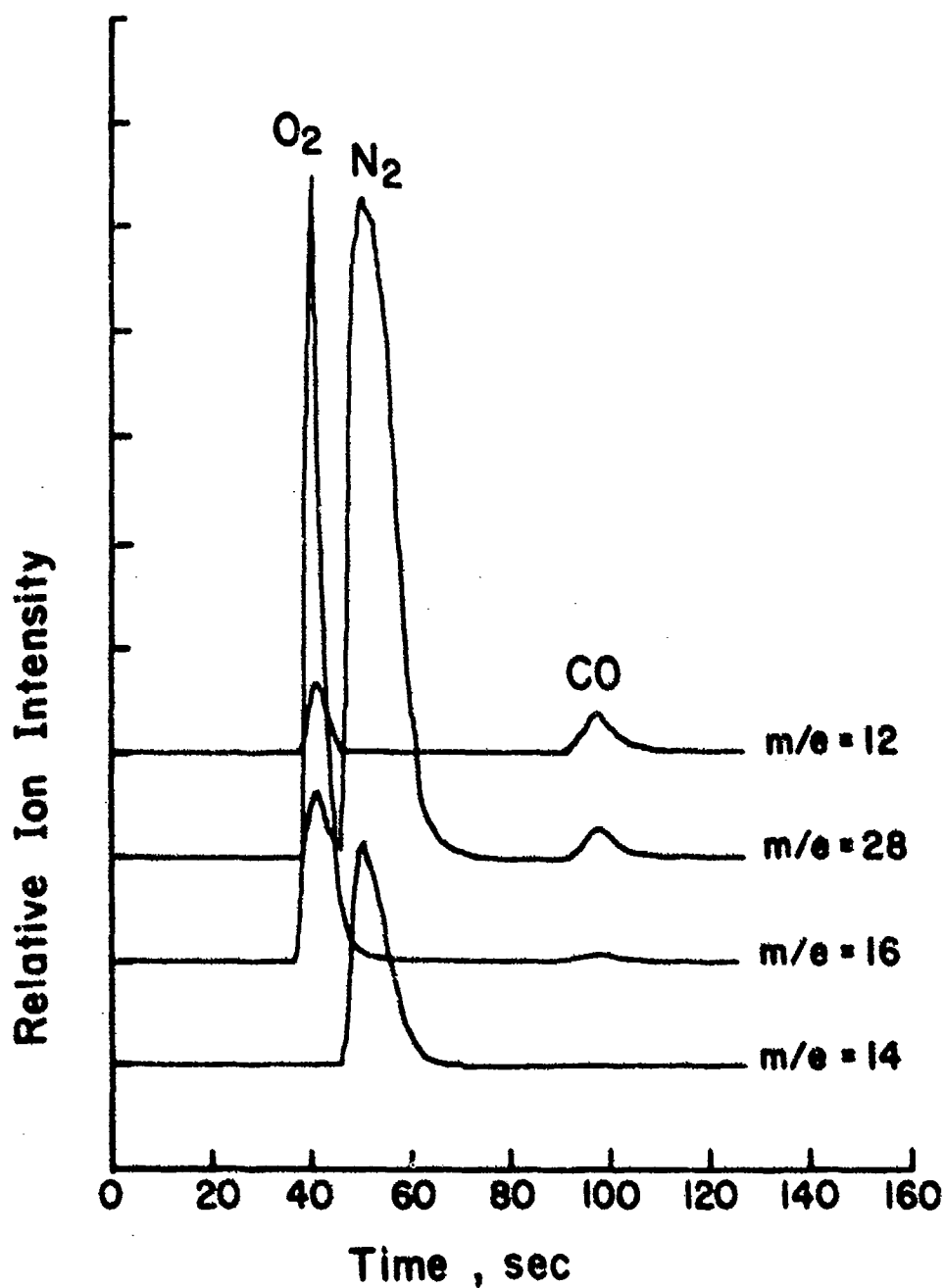


Figure 13. GC-MS Output trace for the analysis of CO. Sample: standard CO-air mixture with a CO/N<sub>2</sub> mass fraction ratio of 0.0712.

analysis of the sample bottles collected during the ramjet combustion tests. The results of these analyses are summarized in Table 3. The extremely low concentration of CO detected in these samples indicates that combustion was essentially 100% complete in these tests. However, these data may be subject to errors arising from the fact that condensible components ( $H_2O$  and fuel) are not quantitatively collected during the sampling process. Also, a valve on one sample bottle (No. 4) developed a leak upon heating during the analysis. As emphasized previously, more accurate ramjet sample analysis requires use of the molecular beam mass spectrometer system.

#### IV. MOLECULAR BEAM MASS SPECTROMETRIC GAS MONITORING SYSTEM

This section describes the construction of a molecular beam mass spectrometric system and several associated units for in-situ analysis of ramjet combustor species. In a molecular beam mass spectrometer, adequate pumping is provided such that after leaving the sampling probe, the sampled gases are transported to the mass spectrometer ion source in the form of a molecular beam. The velocity of the gas remains supersonic within most of the transit region. This high molecular velocity, coupled with the favorable line-of-sight configuration for detection, minimizes inter-molecular collisions and collisions with the wall. For all practical purposes, the sampled gas is completely quenched chemically after leaving the sampling probe. Surface interactions (catalysis, absorption, etc.) are also largely eliminated with this method.



TABLE 3  
 RAMJET SAMPLE ANALYSIS RESULTS

Test No.	Fuel/Air Ratio	Mass Fraction Ratio <sup>a</sup>							Fuel <sup>f</sup>	Comb <sup>h</sup>	Thrust <sup>c</sup>
		O <sub>2</sub>	CO <sub>2</sub>	CO <sup>b</sup>	CO <sup>c</sup>	H <sub>2</sub> O <sup>d</sup>	H <sub>2</sub> O <sup>e</sup>				
1	0	0.227	0.002	NA <sup>g</sup>	NA	0.027	0.027	0			
2.3	0.035	0.151	0.148	0.0025	0.0026	0.047	0.049	0	98.7%	87%	
4	0.048	0.171	0.167	0.0032	0.0035	0.060	0.062	0	98.8%	86%	

- a. The mass fraction ratio for component, i, is expressed as  $(mF)_i / (mF)_{N_2}$ .
- b. Based on the C<sup>+</sup> ion signal (at  $m/e = 12$ ).
- c. Based on the CO<sup>+</sup> ion signal (at  $m/e = 28$ ).
- d. Based on the H<sub>2</sub>O<sup>+</sup> ion signal (at  $m/e = 18$ ).
- e. Based on the OH<sup>+</sup> ion signal (at  $m/e = 17$ ).
- f. Based on the total hydrocarbon ion signal which is the sum of ion signals due to saturated hydrocarbons (at  $m/e = 57, 69$ ), cyclic hydrocarbons (at  $m/e = 70$ ), and aromatics (at  $m/e = 77, 91$ ).
- g. "NA" = not analyzed.
- h. Combustion efficiency calculated:<sup>2</sup> based on the measured CO mass fraction ratio.
- i. Combustion efficiency calculated based on the measured thrust.

The design of a molecular beam mass spectrometer system for the present project was not a simple task because of the many problems which are inherent to the ramjet combustor environment. A ramjet combustor is typically operated at high temperature and high pressure, which is incompatible with the high vacuum conditions and relatively low temperature which are characteristic of a mass spectrometer. In addition, during operation of the ramjet combustor, the entire instrument system is subjected to very heavy vibration, while successful operation of a mass spectrometer requires minimal vibration. The vibration of the combustor, as well as the actual physical displacement of the device which results from the combustion thrust force, makes it very difficult to maintain the mass spectrometer in optimum detection or focus position during a sampling experiment. Another problem is that the sampled combustion gas usually contains a large quantity of soot and other particulate matter. Analysis of such "dirty" samples with an instrument which requires inherently clean conditions presents a formidable problem. We also wanted the sampling probe to be traversable during a combustion test to maximize the quantity of data acquired. This placed extreme requirements on the computer interface as well as on the overall mass spectrometer system.

In addition to the problems just described, there were also several more general concerns which had to be considered in designing a molecular beam mass spectrometer system for sampling a ramjet combustor. One such problem involved the arrangement of the mass spectrometer central vacuum housing, which would

accommodate the mass filter assembly, a partition, the molecular beam skimmer assembly, the beam chopper system, and the cooling and trapping system. Careful design of this housing was required in order to assure the efficient utilization of the vacuum space. Furthermore, the design to be such that the mass filter assembly could be positioned either in-line or perpendicular to the axis of the molecular beam.

Another consideration was the fact that the present mass spectrometer is incapable of differentiating CO from the N<sub>2</sub> which is present in large quantity in the combustor gas sample. The analysis of CO thus required a prior separation using a gas chromatograph system, as already discussed. In the case of the molecular beam, this approach necessitated splitting the beam in order to reserve a fraction of the sampled gas for batch GC-MS analysis. The method of achieving this sample split, as well as the problem of automating the entire analysis sequence via remote control, were certainly major tasks to be solved in the present work.

Still other tasks to be accomplished included the overall construction of the molecular beam system and its supporting frame, as well as the combustor probe flange interface and its alignment, the calibration gas inlet system, the power system and its remote control, the vacuum pumping system, and the safety shut-off system. Each one of these subsystems had to be designed and constructed before the molecular beam mass spectrometer itself could be finally assembled.

## A. Molecular Beam Mass Spectrometer

Figures 14 and 15 show the top and side views, respectively, of the molecular beam mass spectrometer system. This system was designed by taking into account each of the factors previously discussed. The system was subsequently constructed and functionally tested, and shown to be satisfactory. Details of this system and its components will now be described.

The first component of the system which was constructed was the mass spectrometer supporting frame. This frame has overall dimensions of 36 inches x 36 inches x 66 inches (height). A set of four wheels and three adjustable support legs are attached to the bottom of the framework. A bottom plate and an upper plate are employed for the support of the vacuum housing assembly and the entire mass spectrometer pumping system.

The vacuum housing assembly consists of a six-port central vacuum housing, 1, and a vacuum T-section, 6 (the numbers here correspond to those shown in Figures 14 and 15). The central vacuum housing has two 12-inch vertical ports, and four 6-inch horizontal ports, 2,3,4,5. The vacuum T-section 6, is shown attached to port 3 of the central vacuum housing, 1.

Attached to the lower port of the six-port central vacuum housing, 1, (again all numbers refer to Figures 14 and 15 in this discussion) is a central pumping system which consists of a liquid nitrogen cold trap, 7, and a 10-inch diffusion pump. Attached to the lower port of the vacuum T-section, 6, is a side pumping system, 9, which consists of a 4-inch diffusion pump, a liquid nitrogen cold trap, and a pneumatic gate valve. A large

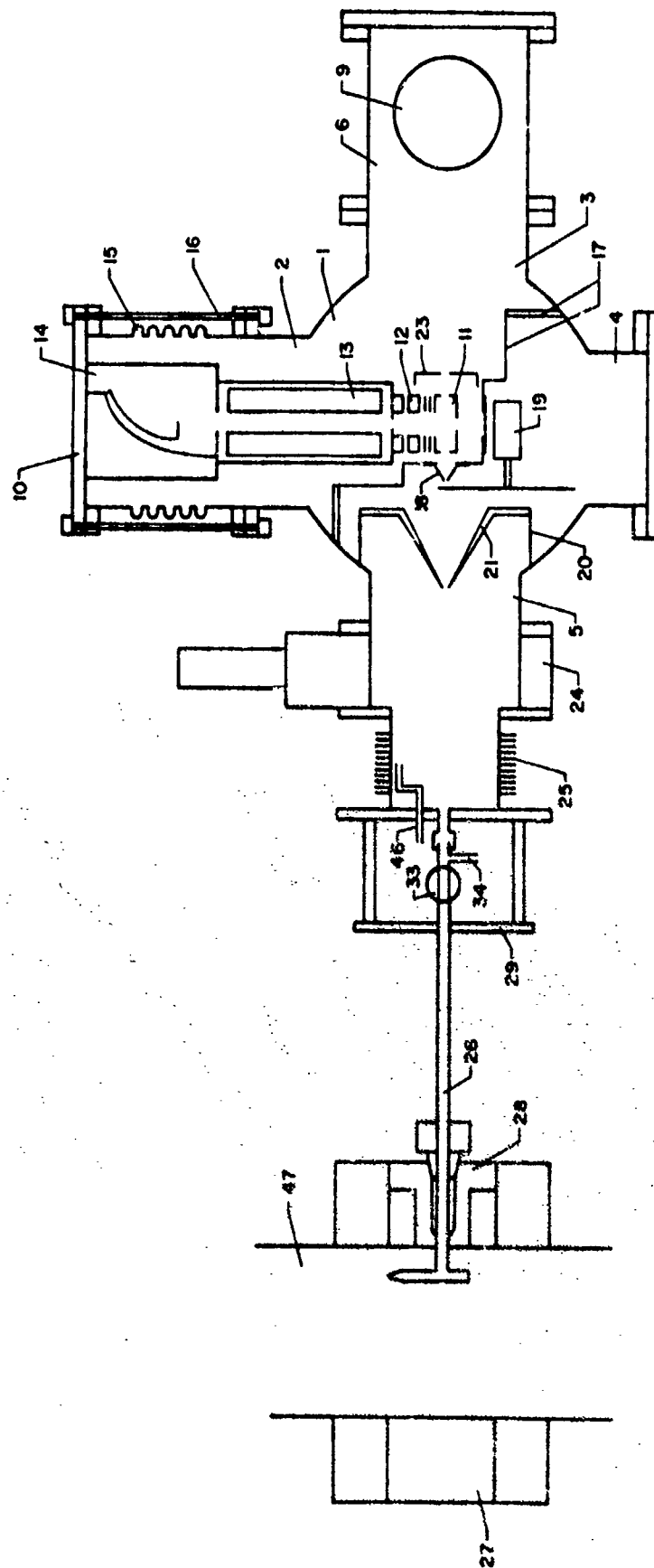


Figure 14. Schematic diagram of the molecular beam mass spectrometer (top view).

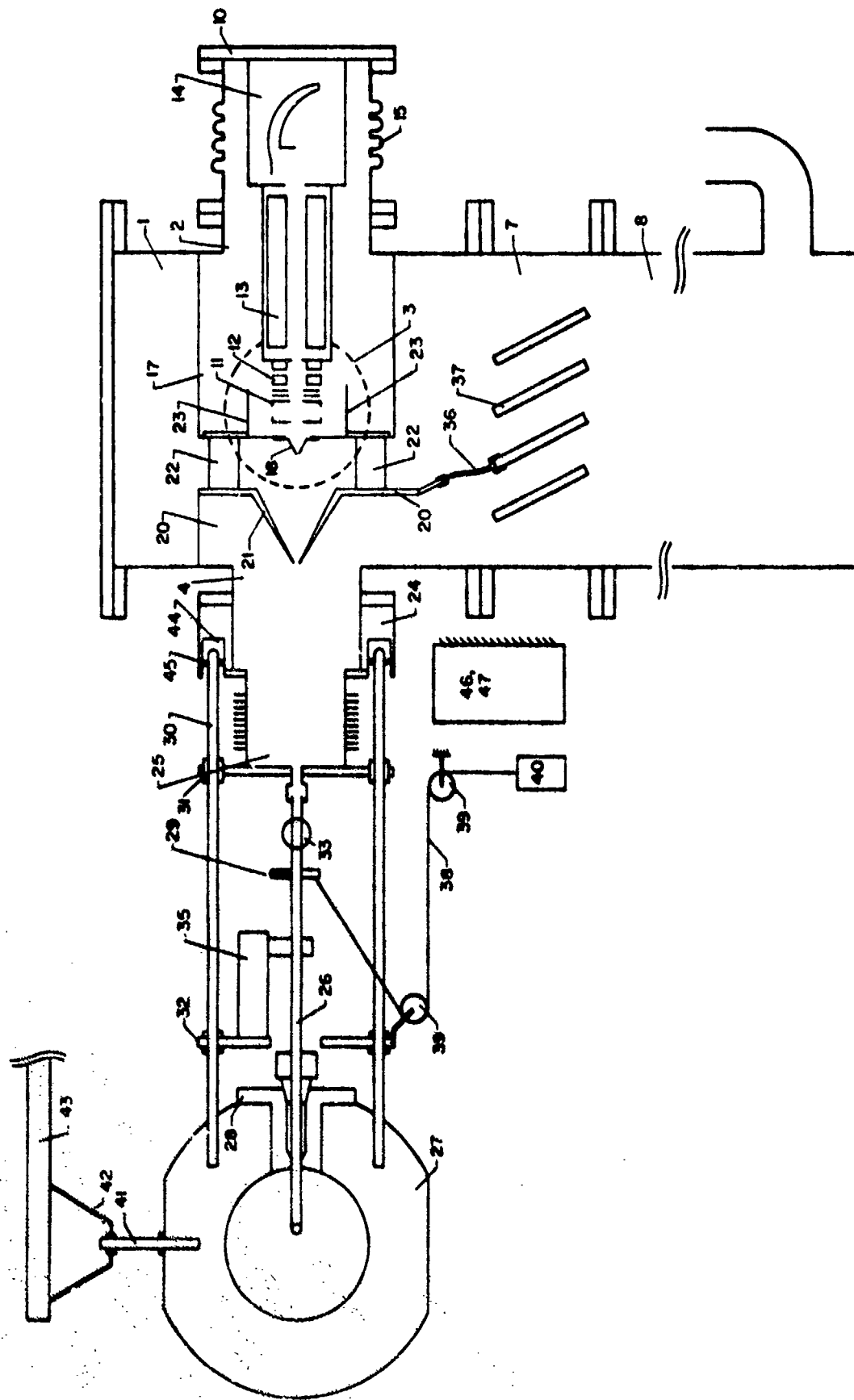


Figure 15. Schematic diagram of the molecular beam mass spectrometer (side view).

FIGURE LEGEND FOR FIGURES 14 AND 15

1. Central 6-port housing
2. Horizontal Port #1
3. Horizontal Port #2
4. Horizontal Port #3
5. Horizontal Port #4
6. Tee housing
7. Liquid N<sub>2</sub>
8. 10" diffusion pump
9. 4" diffusion pump system
10. Quadrupole mass filter assembly
11. Ion source
12. Ion lens assembly
13. Quadrupole mass filter
14. Electron multiplier
15. Formed bellow section
16. Bellow adjustment
17. Partition
18. Skimmer
19. Beam chopper
20. Cold trap plate assembly
21. Copper cone
22. Copper studs
23. Ion source cold trap bracket
24. 4" pneumatic gate valve
25. Welded bellow section
26. Sampling probe
27. Probe flange
28. Probe mounting assembly
29. Probe holding plate
30. Guide rod
31. Bushing
32. Vertical plate
33. Valve
34. Batch inlet tubing
- \*35. Probe drive
36. Braid copper cable
37. Baffle
- \*38. String
- \*39. Pulley
- \*40. Counter weight
41. Probe flange holding rod
42. Bracket
43. Bar
44. Blind hole
45. O-ring
46. Calibration gas inlet tube
47. Combustor
48. Calibration gas inlet and batch sampling system.

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\*not installed at present

mechanical pump (1000 liter/min) serves as the roughing pump for the two diffusion pumps and for a third diffusion pump to be described later.

Inserted into the central vacuum housing through port 2 is an Extranuclear quadrupole mass filter assembly, 10. This assembly consists of an ion source, 11; ion lens assembly, 12; quadrupole mass filter, 13; an electron multiplier, 14; and an end flange for support. All of these components are similar to corresponding items utilized in the other quadrupole mass spectrometer<sup>1,2</sup> except that the ion source, 11, is a crossed-beam type. But with a minor modification, this system can also accept the molecular beam in the axial direction. The whole assembly is supported by a formed bellows section, 15, which is in turn attached to port 2. A set of three adjusting rods, 16, spaced at equal distances apart, as shown in Figure 14, are used for three-dimensional adjustment of the assembly position, in order to align the ion source aperture with the molecular beam.

Referring to Figure 14, the space within the central vacuum housing, 1, is roughly divided into two sections with a partition plate assembly, 17. This assembly consists of a vertical plate which is bent to shape, as shown in Figure 14, and two horizontal plates which are only partially shown in Figure 15 for the sake of clarity. Both the vertical plate and the horizontal plates are carefully shaped to closely mate with the vertical wall of the central vacuum housing, 1, to form an enclosed space within this housing. This enclosed space accommodates the quadrupole mass filter assembly, 13, and is only accessible through the side



pumping system, 9. The space outside this enclosure is pumped by the 10-inch diffusion pump system.

Again referring to Figure 14, there are two openings provided on the vertical plate of the partition assembly, 17. The first hole is covered with a skimmer, 18. This skimmer has an aperture of 0.5-mm diameter, which is aligned with the side opening of the ion source, 11. This skimmer serves to define the final shape of the molecular beam entering the ion source. The second hole is located on the end side of the ion source and is blanked off. Also shown in Figure 14 is a beam chopper assembly, 19, which is supported on the blank flange attached to port 4 by a support which is not shown.

The next item to be described is the cold trap plate assembly, 20, and a copper cone, 21, which is mounted on the assembly. This assembly is supported by the vertical plate of the partition, 17, through two copper studs, 22, in Figure 15. The cone, 21, has an aperture of 1.5-mm diameter which is aligned with the skimmer aperture, 18. The assembly, 20, is box-shaped but with one side open to port 5 and its bottom open to the 10-inch diffusion pump system. The remaining side plates (one on the top and two on the side) are closely mated with the vertical wall of the central vacuum housing, but with a narrow gap (approximately 0.01") in between to minimize the heat transfer through contact. The bottom of the assembly, 20, is physically connected with the baffle plate 37, of the cold trap, 7, through a series of flexible copper cables, 36. During normal operation, with the cold trap, 7, filled with liquid nitrogen, the entire

cold plate assembly, 20, and the cone, 21, are also cooled.

The cold plate assembly and the cone greatly enhance the overall pumping capacity of the mass spectrometer system and help to maintain the cleanliness of the central vacuum housing. The placement of this cone, 21, is such that it serves as a second beam skimmer and assures that any gas sample which failed to enter the aperture of the cone, 21, will be brought into contact with the cone surface and the cold plate assembly. Such contact will cause the condensible components in the gas stream, such as unburned fuel, water, moisture, and soot particles to be deposited on the cold surface of the cone and the assembly, 20. A much cleaner environment in the rest of the central housing space can therefore, be achieved.

In addition to the above-described cryogenic pumping, the cold plate assembly, 20, and the cone, 21, should also assist the pumping of the non-condensable gases, such as air, in the combustor gas sample. After colliding with the cone surface the incoming gas sample is largely confined within the space surrounded by the assembly, 20. Eventually, these gas molecules develop a downward motion toward the trap, 7, and are pumped away, with insignificant backstreaming. The net result is the achievement of additional differential pumping, which allows the central housing outside of the cold plate assembly, 20, to be maintained at a lower pressure for a given gas sample flowrate.

Figures 14 and 15 also show an element, 23, termed "ion source cold trap bracket" which loosely surrounds the ion source, 11. This bracket is made of oxygen-free copper and is mounted on

the vertical plate of the partition, 17, opposite the copper studs, 22. This bracket can also be cooled to a certain degree when the copper studs, 22, are cooled. Any condensible gases, especially water vapor and hydrocarbon fuel which escape the ion source without being ionized will be largely condensed on this bracket. This can help to reduce the background concentrations of water vapor and hydrocarbons, which have been a persistent problem in the previous mass spectrometric analysis.

As shown in Figure 14, port 5 of the central housing is attached to a 4-inch pneumatic gate valve, 24. This valve is open only during operation of the system, and can automatically shut-off when the central housing pressure is raised to an undesirably high level, owing to an excessive gas sampling load, or to a leak.

It is clear from Figures 14 and 15 that the quadrupole mass filter assembly, 10, can be positioned in either crossed or axial relationship with the incoming molecular beam. To convert from the crossed configuration to the axial configuration, the mass spectrometer is merely rotated by 90° once the gate valve, 24, is removed. Of course, the positions of the skimmer, 18, chopper assembly, 19, and the cone, 21, along with the associated components, must also be repositioned. The axial configuration generally affords better detection sensitivity, but the background noise is also increased.

The gas sampling probe, 26, shown in Figures 14 and 15 is the same one used previously and is described in detail in the previous section of this report. This probe is mounted on a

probe flange, 27, which is sandwiched between two Ramjet combustor sections. This probe flange, as well as the flange insert, 28, have also been described in the previous section.

The next item to be described is an interface system for connecting the sampling probe with the mass spectrometer. The design of this interface system is critical because it must allow "line-of-sight" transfer of the sample from the end of the sampling probe to the mass spectrometer, in a molecular beam fashion, so that few collisions of the gaseous species with the walls or with other gaseous species occur. The construction of this interface must be sturdy enough to withstand the vibration of the combustor, while at the same time avoiding transfer of this vibration to the mass spectrometer. Finally, this interface system must also enable the sampling probe to traverse across the combustor freely during the sampling test. The design described in the following is a first attempt to satisfy these criteria.

Perhaps the most important component in the probe-mass spectrometer interface system is a welded bellows section, 25, with two custom-fabricated end flanges. The bellows section (I.D. 4.0 inches; O.D. 5.0 inches; stainless steel) has a total stroke length of 8.48 inches which is adequate for the probe traverse requirement (6 inches). The front end flange of the bellows section, 25, is firmly attached to the gate valve 24. The other flange is connected to and moves with the sampling probe, 26. The valve, 33, shown in the figures is optional and is required only if both molecular beam sampling and batch sampling are desired for each combustor run.

As seen in Figure 14 and 15, a horizontal plate, 29, is employed to firmly attach the sampling probe, 26, to the bellows section, 25. In this arrangement, the end of the probe, 26, is inserted through a hole on the horizontal plate, 29, and is fastened to the plate with two dowel pins (not shown in the figures). This horizontal plate is in turn fastened to the bellows section, 25, with two side bars. The present design will thus allow the horizontal plate and the end flange of the bellows section to be moved concurrently as the sampling probe is traversed.

To reduce the strain on the sampling probe, 26, two horizontal bars, 30, are also provided, as shown in Figure 15. These two bars are threaded on their front section for insertion into the probe flange, 27. A vertical plate, 32, is placed as shown in Figure 15. These two bars are threaded on their front section for insertion into the probe flange, 27. A vertical plate, 32, is placed as shown to enhance the rigidity of the bar structure. The rear section of these bars has a smooth surface for guiding the movement of the bellows section, 25. Two bushings, 31, are provided to facilitate this movement, which is driven by a probe-drive unit, 35.

It is conceivable that vibration of the probe flange, 27, during a combustion test may cause excessive vibration of the horizontal bars, 30, especially the rear sections of these, if the bars are freely suspended. This problem may be somewhat resolved by inserting the horizontal bars into two blind hole cavities, 44, which are provided on the gate valve, 24. An O-

ring, 45, is shown in each of these cavities to serve as a damping device.

During the initial installation, and prior to the actual sampling, the gate valve, 24, is kept closed while the trapped ambient air within the bellows section, 25, is pumped away through a roughing port of the gate valve, 24. Once vacuum has been achieved inside the bellows section, atmospheric pressure is inevitably applied to the flange surface of the bellows section. This imbalance of forces is countered by a counterweight, 40, which is attached with a cord, 38, the other end of which is tied to the horizontal plate, 29. Two pulleys, 39, are also employed as shown in Figure 15.

When the probe flange, 27, is not installed on the Ramjet combustor, 47, it is supported by a threaded bar, 41, which is mounted on a bracket, 42. This bracket is in turn mounted on an adjustable bar, 43, which is part of the mass spectrometer supporting framework. This arrangement greatly facilitates the alignment of probe flange with the Ramjet combustor and positioning of the mass spectrometer. Once the probe flange is properly attached to the Ramjet combustor, the bar, 41, can be released from the probe flange and the bar, 43, retrieved.

#### B. Calibration Gas Inlet System

For the calibration of the mass spectrometer response in order to accomplish molecular beam analysis, a calibration gas inlet system is provided. This system is shown schematically in Figure 16. It consists of an insulated oven box, (1 in this figure), positioned beneath the gate valve (24 in Figure 15).

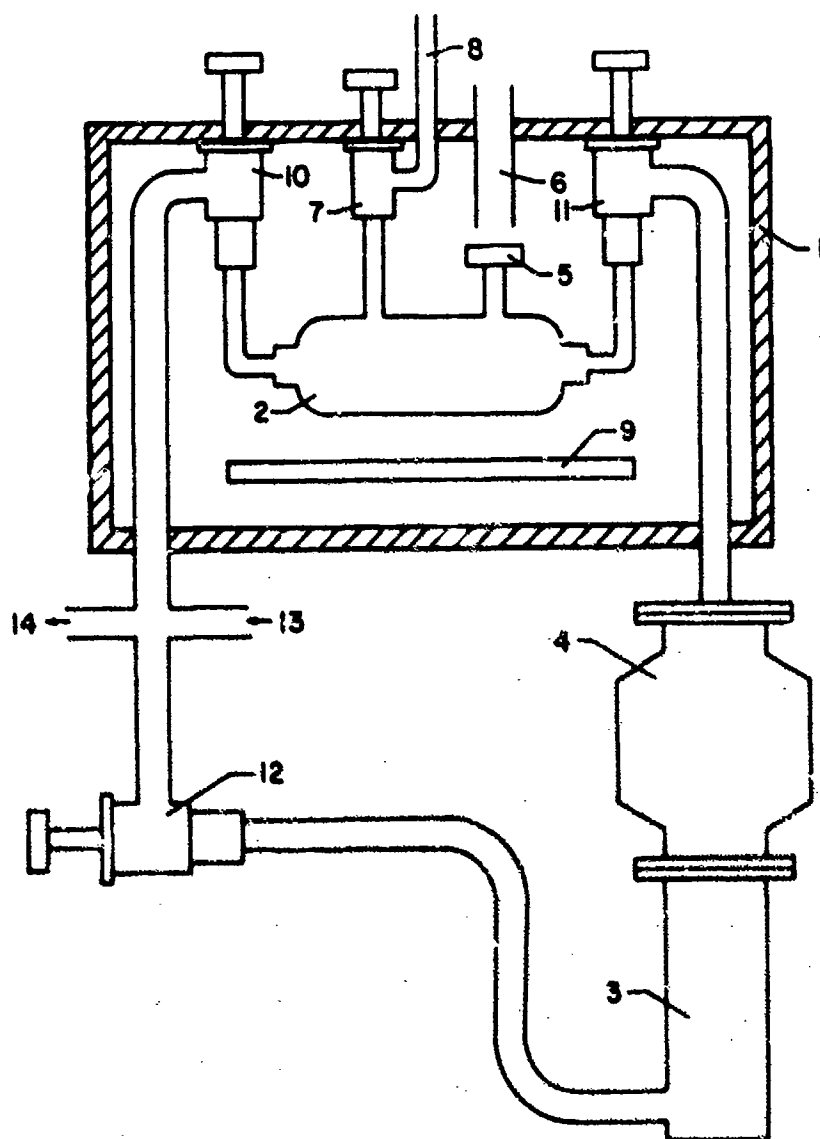


Figure 16. Schematic diagram of the calibration gas inlet system for the molecular beam mass spectrometer.

# FIGURE LEGENDS FOR FIGURE 16

<u>Item</u>	<u>Description</u>
1	Oven Box
2	S.S. reservoir (300 cc)
3	2" diffusion pump
4	Cold trap
5	Injection port
6	Syringe guide
7	Metering valve
8	Outlet tubing
9	Heating Plate
10	Roughing valve
11	Diffusion pump valve
12	Diffusion pump outlet valve
13	Port for pumping the batch GC system
14	To mechanic pump



Located within this box is stainless-steel reservoir 2, having a volume of 300 cc. A small diffusion pump system which consists of a 2-inch diffusion pump, 3, and a liquid nitrogen trap, 4, is provided to evacuate this reservoir. The sample inlet to this reservoir is an injection port, 5, which receives a premeasured quantity of standard sample, including air, CO, CO<sub>2</sub>, H<sub>2</sub>O and liquid fuel. Note that the injection port, 5, is positioned deep inside the oven in order to avoid any cold spots which may cause unwanted sample condensations. The tube, 6, is provided to guide the entry of the injection syringe. Once the injected sample is properly vaporized, the standard mixture is then withdrawn through the metering valve, 7, and the outlet tubing, 8, for analysis.

The outlet tubing, 8, is connected to a stainless-steel tube (46 in Figure 14), which can rotate via a feed-through in the end flange of the bellows section (25 in Figure 14). This tube is bent to shape, as shown in Figure 14. Prior to the calibration test, this tube is rotated such that the front portion of the tube, will be positioned along the center line, in alignment with the cone (21 in Figure 14) and the skimmer (18 in Figure 14). This is important because the gas calibration must be conducted in the same manner as the real molecular beam sampling, so that any potential discrimination caused by the sampling can be eliminated. After the calibration test, the tube (46 in Figure 14) can then be rotated back to its recessed position as shown in the figure.

### C. Batch Sampling and Gas Chromatograph Analysis System

As mentioned previously, due to the inability of the low resolution mass spectrometer used in the present system to differentiate the ions  $\text{CO}^+$  and  $\text{N}_2^+$ , the analysis of the CO gas must be carried out in a batch mode using a gas chromatograph (GC), which physically separates the CO from the  $\text{N}_2$  gas prior to mass spectrometric detection. The methodology for this GC-MS operation is expected to be similar to that established previously, as described in Section III. However, for the molecular beam mass spectrometer operation, two major objectives are sought. First, the system design must place maximum emphasis on automation, so that the entire sequence of gas sampling, sample transfer and GC-MS analysis can be carried out automatically, through a simple control operation at the remote station. Secondly, the system should make use of a sample concentrating procedure in order to increase the CO detection sensitivity, without compromising the performance of the GC.

Figure 17 shows a schematic diagram of a batch sampling and gas chromatographic analysis system designed with the two objectives just mentioned in mind. The entire system is housed in a box (46 in Figure 15) which is located under the probe gas inlet gate valve (24 in Figure 15). The major components of this system include the solenoid valves, 1-11; electrically-actuated 6-port valve, 12; GC column, 13; and a double cylinder, 14. The detailed operating procedure for this system is summarized in Table 4. An unique feature of this arrangement, as seen in this table, is that each step in the procedure merely involves the

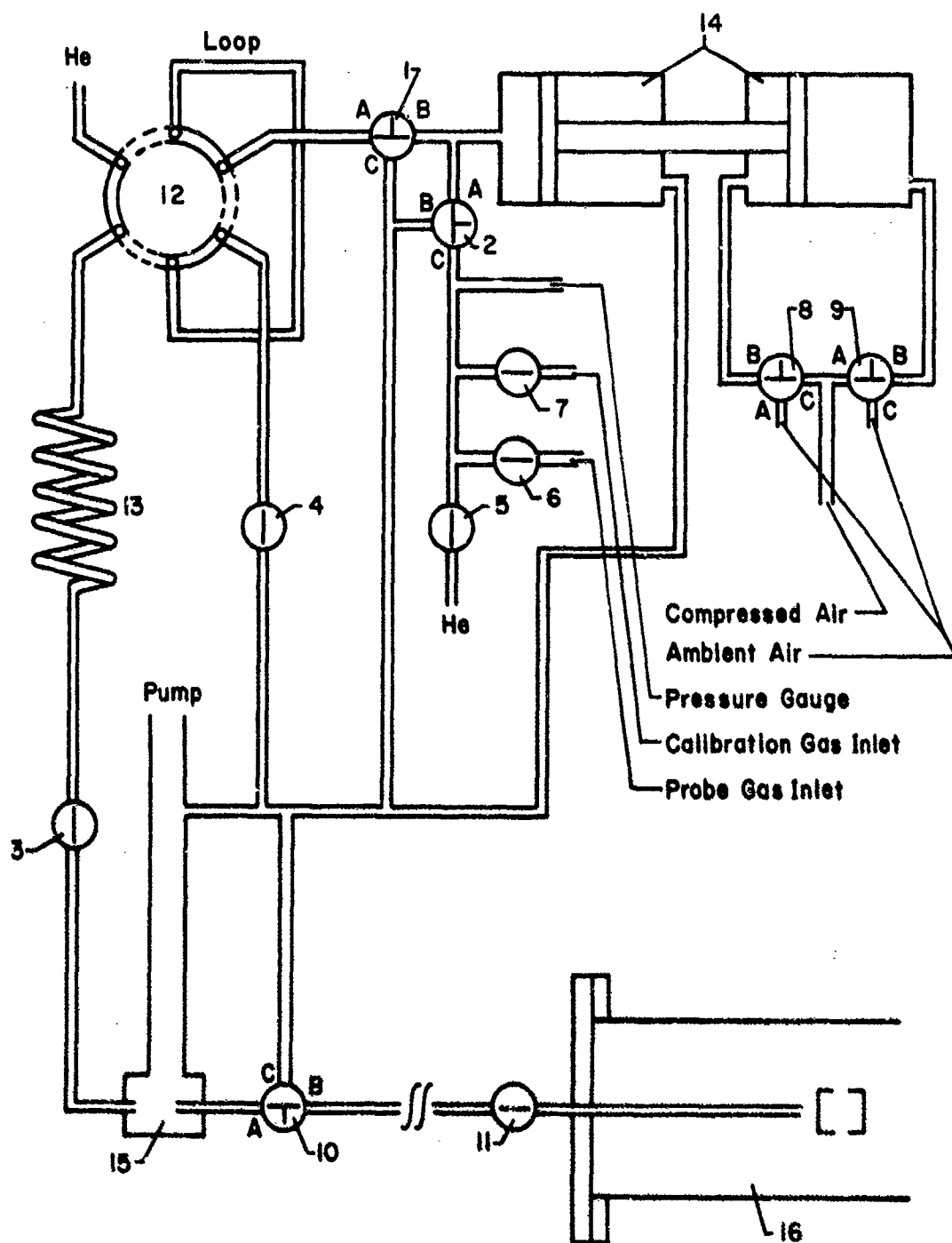


Figure 17. Schematics of the Batch Sampling and GC Analysis System

- 1-11 Solenoid Valves
- 12 6-port valve
- 13 GC column
- 14 Double cylinder
- 15 Gas splitter
- 16 Mass spectrometer

opening or closing of the valves, 1-12, which can be readily achieved under computer control in an automatic fashion. However, before such total automation can be achieved, manual control will likely still be required, at least for the near future.

The procedures listed in Table 4 include the operations of both system calibration and the actual ramjet sample collection and analysis. Since these two operations are similar, only the later one will be described here.

As seen in Figure 17, the double cylinder, 14, consists of a front cylinder and a back cylinder. The back cylinder drive the cylinder piston while the front cylinder acts as a sample reservoir. Prior to sample collection, the cylinder is moved to the right while the sample reservoir is evacuated. At this time, the loop within the 6-port valve is also evacuated by turning valve 12 to the by-pass position, and valve 4 to the open position. At the end of the evacuation period, valve 4 is then closed.

To start sample collection, valves 6 and 2 are opened. This allows the sample gas from the sampling probe to flow into the reservoir. Upon completion of sample collection, these two valves are then closed.

At the end of sample collection, the pressure of the sampled gas within the reservoir is still very low. The sampled gas must be concentrated before it is analyzed. This sample concentration is achieved with the following steps: 1) de-energize valves 2 and 4; 2) energize valve 1; 3) energize valves 8 and 9. After these

TABLE 4  
CO BATCH ANALYSIS PROCEDURE

Operation <sup>1</sup>	Valve No.											
	1	2	3	4	5	6	7	8	9	10	11	12
I. Stand-by (idle)	D <sup>2</sup>	D	D	D	D	D	D	D	D	D	D	by-pass <sup>3</sup>
II. Calibration												
1. Stand-by	D	D	D	D	D	D	D	D	D	D	D	by-pass
2. Carrier gas on			E <sup>2</sup>							E		
3. Gas to M.S.											E	
4. Calibration gas on	E	E		E			E					
5. GC Run start												loop <sup>3</sup>
6. GC Run End												by-pass
7. Pump Down	D	D					D					
8. Purge	E	E			E							
9. Pump Down	D	D			D							
10. Stand-by			D	D						D	D	
III. Probe Sample Analysis												
1. Stand-by	D	D	D	D	D	D	D	D	D	D	D	By-pass
2. Carrier gas on			E							E		
3. Gas to MS											E	
4. Pump down	D	D		E								
5. Purge	E	E			E							
6. Pump down	D	D			D							
7. Probe gas on <sup>4</sup>	E			D		E						
8. Start sample collection <sup>5</sup>		E										
9. End Sample collection		D										
10. Sample compression								E	E			
11. GC Run start												loop
12. GC Run stop												by-pass
13. Pump down	D			E		D		D	D			
14. Purge	E	E			E							
15. Pump down	D	D			D							
16. Stand-by			D	D						D	D	

#### Foot Notes To Table 4

1. Blanks in the table (that is, no letter designation) for a given operating step indicate that the valve position remains unchanged from the previous step.
2. "D" = de-energized; "E" = energized. For a two-port valve, the status ports are in communication when the valve is energized, and isolated when the valve is de-energized. For a three-port valve (ports A, B, C as indicated), ports A and B are in communication when the valve is energized; ports B and C are in communication when the valve is de-energized.
3. In "by-pass" position the gas flow follows the solid line path, in "loop" position the gas flow follows the dashed-line path (see Figure 18).
4. Ramjet combustion is started after this step.
5. Ramjet combustion is terminated after this step.

steps, the cylinder piston will be moved to the left until it stops when the cylinder drive force (i.e., the compressed air pressure) is balanced by the pressure exerted by the compressed sample gas. A significant portion of the gas sample is thus transferred from the reservoir to the loop of the 6-port valve 12. With this arrangement, concentration of the CO gas by a factor of ten or more can be achieved. This results in an increase in the CO detection sensitivity without compromising the performance of the GC.

Following the gas concentration procedures just described, the 6-port valve, 12, is switched to a new position (gas flow along the dashed line in Figure 17), which allows the gas sample trapped within the loop to be swept by the He carrier gas into the GC column, 13. The CO gas separated by the column is subsequently introduced into the mass spectrometer for analysis. The entire sample collection-concentration-analysis procedure is expected to require about 10 minutes after all operating steps are properly optimized.

#### D. Evaluation of the Completed Molecular Beam Mass Spectrometer System

Toward the latter part of this contract, the construction of the molecular-beam mass spectrometer system was completed. This system was then subjected to a series of functional checks. In this section a brief report on the results of these checks will be provided.

The first check conducted was a leak test of the entire vacuum housing. One leak was uncovered and subsequently

repaired. The 10" and 4" diffusion pump systems were subsequently checked. All of the associated valving, cooling, and gaging stems were also examined and found to function properly. An excellent vacuum level ( $1 \times 10^{-7}$  torr) was achieved in the vacuum housing with the pumping systems as indicated.

A safety protection system was also incorporated into the present mass spectrometer system. Any decrease of the cooling water supply, of the electrical supply to the diffusion pump heaters, or of the vacuum, triggers this safety protection system, and shuts off all mass spectrometer electronics and closes several critical isolation valves. All these safety features were tested by producing simulated failure conditions. Satisfactory results were found in all these tests.

To achieve the best sample detection sensitivity, the ion source (11 in Figure 14) gas inlet aperture should be properly aligned with the apertures of the copper cone, 21, the skimmer, 18, and the center of the molecular beam as it leaves the sampling probe. This alignment was accomplished successfully by using a pilot laser beam.

The next item which was tested was the quadrupole mass filter system. For these tests, the quadrupole controls and the associated electronic equipments which were located in AFWAL/APL were temporarily relocated to WSU. The new quadrupole mass filter system was properly tuned and operated successfully. Several mass spectra were obtained for actual samples (JP-4, Ar, etc.), which had been introduced either with the sampling probe or from the sample reservoir (2 in Figure 16). The performance



of the new mass spectrometer system was found to be satisfactory as judged by the mass spectra obtained.

In the mass spectrometer test just described, the quadrupole control cabinet was placed near the mass spectrometer using standard 10-ft cables for their interconnection. Later, some of these short cables were replaced with longer (50-ft) cables in order to study the feasibility of placing the control cabinet for the instrument at a remote position (in the control room) for ease of control. Unfortunately, these long cables were found to induce a large imbalance in the RF-DC quadrupole fields. This problem cannot be corrected without extensive instrument modifications. An additional problem with the long cables is the possibility of noise pick-up in the long analog ion-signal transfer line. On the basis of these findings, we decided that the quadrupole control cabinet must be placed adjacent to the mass filter for the best mass spectrometer operation. Although some inconvenience in ease of control may result from this requirement, we do not expect a major problem because we anticipate that the mass spectrometer operation will be controlled mainly by the interfaced computer.

As described previously, the partition plate assembly (17 in Figure 15) was used to divide the central vacuum housing (1 in Figure 15) into two sections. The first section is pumped by the 10-inch diffusion pump system and thus termed 10-inch chamber section. The second section is pumped by the 4-inch diffusion pump section (thus termed 4-inch chamber section) and is used for housing the quadrupole mass filter. The ratio of the 10-inch

chamber pressure to the 4-inch chamber pressure generally falls within the range, 10-40. The magnitude of this ratio is expected to var., depending upon the aperture size of the skimmer unit (18 in Figure 15).

After the initial success of the mass spectrometric functional checks, the entire molecular beam assembly was relocated to the AFWAL/APL facility site. New electric lines, a new water supply line, and an exhaust system were installed on this site. This permitted the molecular beam assembly to be reactivated. Several functional checks previously conducted were again repeated and were found to be satisfactory. The operation of the assembly was also subsequently carried out using the digital mass programmer (DMP) and demultiplexer (DM) units with success.

The next task accomplished was interfacing the molecular beam system with the existing computer system (MODCOM) for automated data acquisition and mass spectrometer operation control. Numerous hardware interface line connections were made. Several previously programmed software routines were employed with a few minor modifications. Successful computer-interfaced mass spectrometric operation was achieved. The data acquisition program which was tested allowed plots of all sample concentration raw data to be displayed after each run. These data can be subsequently processed to yield the information required for the sample concentration calculation.

The initially constructed calibration gas inlet system (Figure 16) was next subjected to experimental evaluation. As

stated previously, this system is used for calibrating the mass spectrometer response in order to measure the concentration of the combustion species. Among the components successfully tested were the mechanical pumping system for the reservoir, and the heating and temperature sensing components of the oven box. The 2-inch diffusion pump was found defective but was repaired subsequently. The original outlet tubing (8 in Figure 16) was replaced with coiled copper tubing to facilitate the heating and temperature control of this gas transit line.

Upon completion of the examination of the calibration gas inlet system, a series of gas calibration tests were carried out. In these tests several standard mixtures consisting of water, JP-4, CO and CO<sub>2</sub> (in air), having mass fractions relative to the mass fraction of N<sub>2</sub> of 0.250, 0.200, 0.0712 and 0.112, respectively, were prepared and stored in the reservoir (2, Figure 16). The temperature of the reservoir as well as the oven box was maintained at 150°C in order to assure the vaporization of all injected liquid sample (water and JP-4). The prepared mixtures were then introduced into the mass spectrometer, which was operated in the selected-ion-monitoring mode with data acquired by the interfaced computer.

As seen in Figures 14 and 15 a skimmer, 18, and a copper cone, 21, are placed inside the 6-port central housing section of the molecular beam system. The aperture diameters of these two elements are 0.5 mm, and 1.0 mm, respectively. One purpose of these two elements is to achieve differential pumping. This is

required because the amount of sample gas flow during the ramjet combustion test is typically several orders of magnitude larger than what is acceptable in the mass spectrometer. However, in the gas calibration test the amount of gas flow is much smaller. As a result, the observed detection sensitivity was too low and could not be easily remedied by repositioning the calibration gas inlet tube (46 in Figure 14). In one later test both the skimmer and the copper cone were temporarily removed. Much higher detection sensitivity was achieved. The signal response for all compounds tested was also quite linear over the concentration range applied. This experimental finding suggested that at least the skimmer will need to be made movable in order to cope with different gas sampling flow conditions. More experimental investigation is required in this regard.

#### V. MEASUREMENT OF THE SIMULATED FUEL (ARGON)/AIR MIXING PROFILE

This task entailed in-situ measurement of the simulated fuel/air mixing profiles in the ramjet combustor flowfield. For all of the tests conducted during the contract period, an existing dual-inlet ducted rocket combustor was employed. The cross section of the ducted inlet is of rectangular shape and has the same cross-sectional area as that of the circular dual-inlet section employed previously. The air introduced through these inlets was mixed with the argon simulated fuel, injected along the center line of the combustor, and subsequently ejected into the combustor chamber (15 inches long, nominal I.D. 4 inches). A sampling probe was allowed to traverse across the combustor

chamber continuously. The sampled gas mixture was then analyzed in-situ by the mass spectrometer system, with the data being acquired and reduced by the interfaced computer system.

During the final contract period, a new series of cold flow sampling tests was conducted using the facilities described above. The variable experimental parameters in these tests included the air pressure (30.5 and 35.5 psi); inlet pressure (200, 120, and 80 psi); and the probe positions (15, 13.9, and 9.3 inches downstream from the duct inlet). The Argon mole fraction profiles were automatically obtained using either the dual probe traverse or the recently modified single traverse mode. These profiles exhibited complicated patterns which were highly dependent on the inlet air and fuel pressures employed. The degree of the fuel-air mixing appears to be more efficient in comparison with the dump combustor configuration previously employed. In view of the complexity of the combustor flowfield many more sampling tests are now required with the combustor rotated to different orientations in order to fully characterize the fuel-air mixing flowfield in this device.

During the final contract period, the laboratory computer system located in Bldg. 450 was also considerably upgraded. Along with this, a new interface hardware system and the software package for data acquisition and reduction were installed. Considerable effort was expended in interacting with the computer personnel on the design and testing of these software and hardware systems.

Toward the latter portion of this final project period, yet

another series of simulated ramjet combustor sampling tests were carried out. In these tests, the variable experimental parameters included the air pressure, the inlet (Argon) pressure and the location of the sampling probe downstream from the duct inlet. Furthermore, the angle between the traversing probe and the horizontal plane can also be varied by rotating the combustor section. Data were obtained for probe angles of  $0^\circ$ ,  $45^\circ$ ,  $90^\circ$ , and  $135^\circ$ . While the analysis of these data was not completed at the conclusion of the contract, we anticipate that the data derived would yield a three-dimensional fuel-air mixing pattern within the combustor for each combination of air and Argon pressure.

## VI. CONCLUSIONS AND RECOMMENDATIONS

During the term of the present contract, several major achievements have been realized. These include, (a) the successful design, fabrication and testing of a markedly improved gas sampling probe for use with high temperature combustion plasmas; (b) successful development and implementation of a batch sampling system for combustor sampling; and (c) successful design, construction, and preliminary evaluation of a molecular beam mass spectrometer system for monitoring gaseous species in combustors. The first two of these tasks were completed during the period of this contract, while considerable work remained, at the conclusion of the contract, to fully evaluate and demonstrate the molecular beam mass spectrometer system.

Considering the enormous range of gaseous species

concentrations, gas pressures and other related parameters which will undoubtedly be characteristic of various combustor systems, it is impossible to foresee all of the minor adjustments in the molecular beam mass spectrometer system which may be necessary to achieve optimum detection sensitivity and operating conditions. As noted in this report, it would be desirable in the near term, to determine the effects of the skimmer position on the system response. Optimization of such experimental parameters can only be achieved by conducting a series of actual combustor sampling experiments using the molecular beam mass spectrometer system. Such tests will likely reveal that various other instrumental parameters must also be adjusted to achieve successful sampling and detection with the molecular beam mass spectrometer system.

As also mentioned in the present report, just prior to the completion of this contract, a full set of angle-resolved probe measurements was accomplished as part of a series of simulated ramjet combustor sampling tests. However, there was insufficient time to reduce the data obtained in these experiments before the contract terminated. Obviously, the Air Force should proceed to reduce these data since it is expected that this would yield the first three-dimensional fuel-air mixing pattern which has been obtained for this combustor.

Finally, it should be noted that full realization of the capabilities of the molecular beam mass spectrometer sampling system will require computer data acquisition and reduction. While some progress was made in this respect, as mentioned in the report, considerable work on this task remains to be

completed. This portion of the project was mostly outside of Wright State's responsibility.



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